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- (54) **PROCESSES FOR PRODUCING HIGH PROPYLENE CONTENT PEDM USING TETRAHYDROINDACENYL CATALYST SYSTEMS**
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- (60) Provisional application No. 62/644,971, filed on Mar. 19, 2018.

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(58) **Field of Classification Search**

CPC ... C08F 210/18; C08F 4/65927; C08F 4/6592
See application file for complete search history.

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Primary Examiner — Caixia Lu

(57) **ABSTRACT**

The present disclosure provides methods for producing an olefin polymer by contacting a C₃-C₄₀ olefin, ethylene and a diene with a catalyst system including an activator and a metallocene catalyst compound comprising a substituted or unsubstituted indacenyl group and obtaining a C₃-C₄₀ olefin-ethylene-diene terpolymer typically comprising from 1 to 35 mol % of ethylene, from 98.9 to 65 mol % C₃-C₄₀ olefin, and, optionally, from 0.1 to 10 mol % diene. Preferably, a propylene-ethylene-ethylidene norbornene is obtained.

(56)

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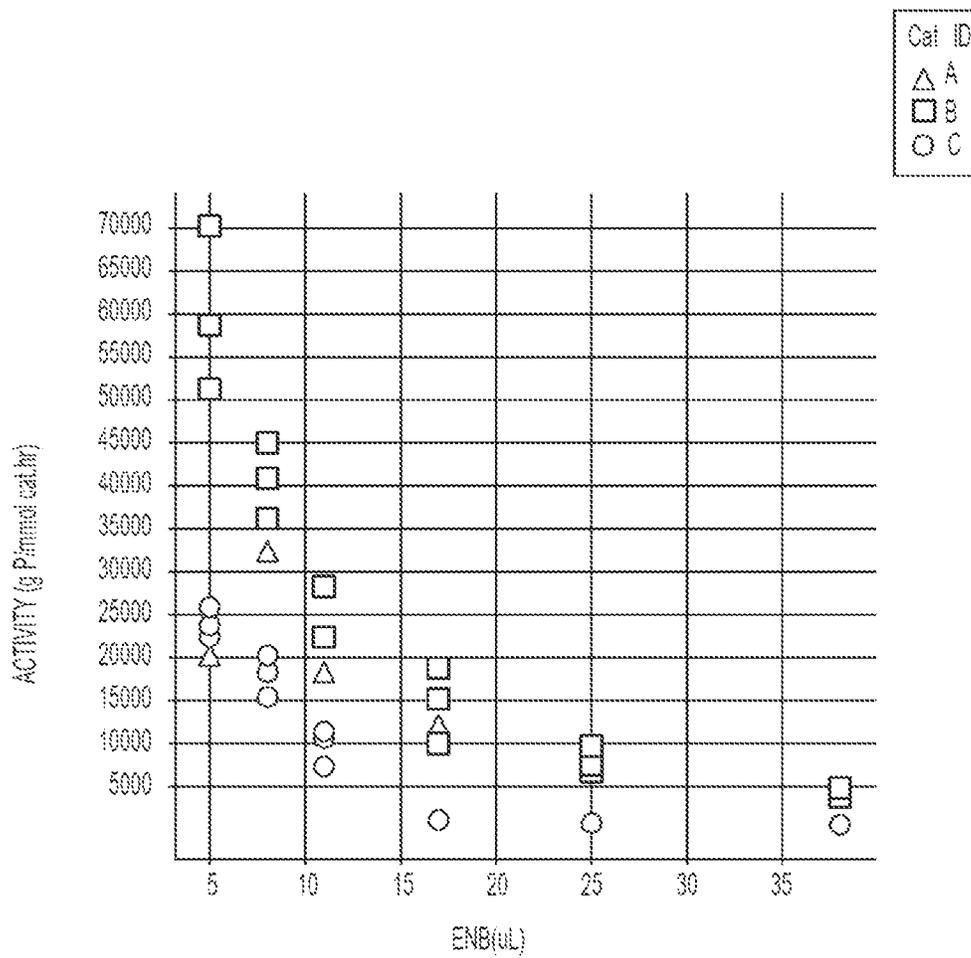


FIG. 1

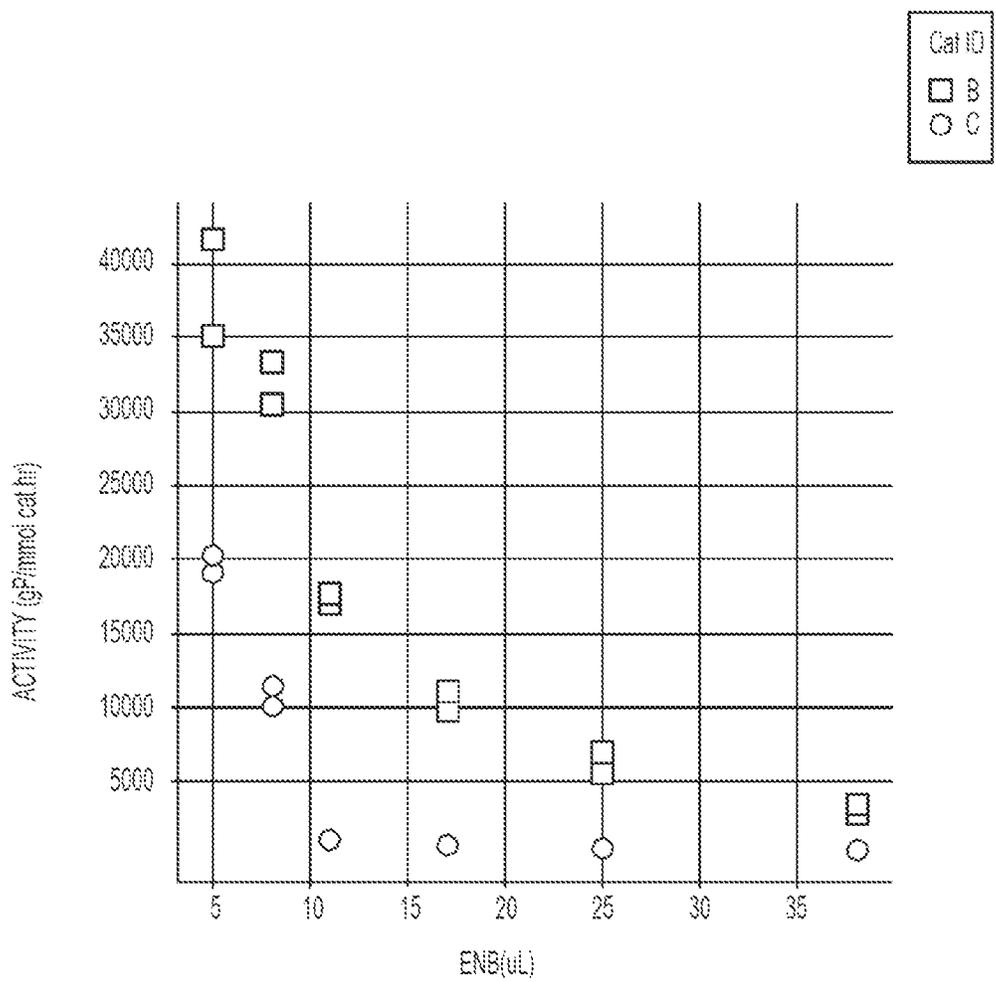


FIG. 2

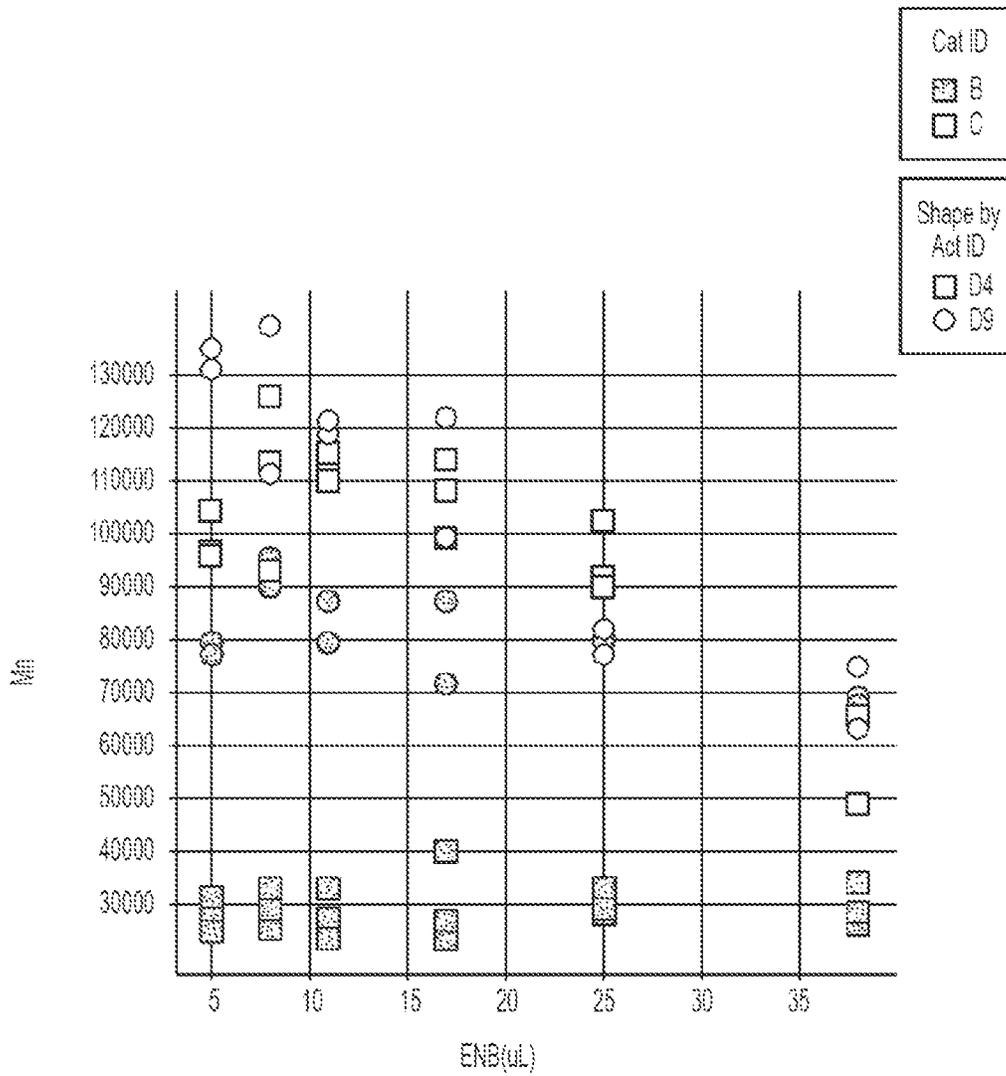


FIG. 3

1

**PROCESSES FOR PRODUCING HIGH
PROPYLENE CONTENT PEDM USING
TETRAHYDROINDACENYL CATALYST
SYSTEMS**

PRIORITY CLAIM

This application is a Divisional of U.S. Ser. No. 16/356,588 filed Mar. 18, 2019 which claims priority to and the benefit of U.S. Ser. No. 62/644,971, filed Mar. 19, 2018 which is incorporated by reference in its entirety.

STATEMENT OF RELATED CASES

This application is related to U.S. Ser. No. 15/145,314, filed May 3, 2016, now U.S. Pat. No. 9,796,795.

This application is also related to PCT/US2015/067582, filed Dec. 28, 2015.

This application is also related to PCT/US2015/067582 filed Dec. 28, 2015 which claims priority to and the benefit of U.S. Ser. No. 62/103,372, filed Jan. 14, 2015.

This application is also related to PCT/US2015/067586 filed Dec. 28, 2015 which claims priority to and the benefit of U.S. Ser. No. 62/103,372, filed Jan. 14, 2015.

This application is also related to PCT/US2015/067587 filed Dec. 28, 2015 which claims priority and the benefit of U.S. Ser. No. 62/103,372, filed Jan. 14, 2015.

This application is also related to PCT/US2016/021751, filed Mar. 10, 2016 which claims priority to and the benefit of U.S. Ser. No. 62/149,799, filed Apr. 20, 2015.

This application is also related to PCT/US2016/021748, filed Mar. 10, 2016 which claims priority to and the benefit of U.S. Ser. No. 62/149,814, filed Apr. 20, 2015.

This application is also related to U.S. Pat. No. 9,803,037.

FIELD

The present disclosure provides catalyst systems and methods for producing C_{3+} olefin-ethylene-diene polymers.

BACKGROUND

Olefin polymerization catalysts are of great use in industry. Hence, there is interest in finding new catalyst systems that increase the commercial usefulness of the catalyst and allow the production of polymers having improved properties.

Catalysts for olefin polymerization are often based on cyclopentadienyl transition metal compounds as catalyst precursors, which are activated either with an alumoxane or with an activator containing a non-coordinating anion. A typical catalyst system includes a metallocene catalyst and an activator, and an optional support. Many metallocene catalyst systems can be used in homogeneous polymerizations (such as solution or supercritical) and supported catalyst systems are used in many polymerization processes, often in slurry or gas phase polymerization processes.

Propylene-ethylene-diene terpolymers are of industrial interest because they can have suitable properties for use in blends and films, such as tire treads and power transmission belts. Conventional catalyst systems can produce Propylene-ethylene-diene terpolymers having a sufficient glass transition temperature (T_g) to provide wet traction and rolling resistance/tread wear when used as a tire tread. Nonetheless, conventional catalyst systems used to produce Propylene-ethylene-diene terpolymers have low catalyst activity such that use of these catalyst systems is not commercially viable

2

(e.g., the catalyst activity of such catalyst systems is 30,000 (g polymer/mmol catalyst/hour) or less.

WO 2004/013149 A1 discloses group 4 metal constrained geometry complexes of tricyclic 4-aryl substituted indenyl ligands, esp. 1,5,6,7-tetrahydro-4-aryl-s-indacen-1-yl ligands, where the tetrahydro-s-indacene is substituted in the 4 position with a C₆₋₁₂ aryl group, and is preferably not substituted in the 5, 6, or 7 position, and if substituted in the 5, 6, or 7 position, is substituted by at most only one substituent at each position.

U.S. Pat. No. 6,420,507 discloses substituted tetrahydro-s-indacenyl transition metal complexes (such as Examples H to N), where the tetrahydro-s-indacene is not substituted at the 5, 6, or 7 position and is substituted at the 2 and/or 3 position.

EP 1 120 424 (and family member U.S. Pat. No. 6,613,713) disclose tert-butylamino-2-(5,6,7-tetrahydro-s-indacenyl)dimethylsilyl titanium dichloride indenyl ligands as polymerization catalyst where the tetrahydro-s-indacene is not substituted at the 5, 6, or 7 position.

WO 2001/042315 discloses dimethylsilylene(t-butylamido)(2-methyl-tetrahydro-s-indacenyl)Ti(CH₂SiMe₃)₂ (see examples 27 and 28, and compounds IB5 and IB5' in claim 21) as polymerization catalysts where the tetrahydro-s-indacene is not substituted at the 5, 6, or 7 position.

WO 98/27103 discloses dimethylsilylene(t-butylamido)(2-methyl-tetrahydro-s-indacenyl)TiCl₂ (see example 1) and others as polymerization catalysts where the tetrahydro-s-indacene is not substituted at the 5, 6, or 7 position.

U.S. Pat. No. 9,803,037 discloses substituted tetrahydro-as-indacenes and a method to produce substituted or unsubstituted tetrahydro-as-indacenes.

US 2016/0244535 discloses monocyclopentadienyl transition metal compounds comprising a tetrahydroindacenyl group (such as tetrahydro-s-indacenyl or tetrahydro-as-indacenyl).

U.S. Pat. No. 9,023,906 (US 2014/0088214), comparative example 1, discloses a propylene-ethylene-ENB terpolymer having a T_g of -27.5° C. and Mw/Mn of 4.7 produced using triphenylcarbenium tetrakis(pentafluorophenyl) borate and Cs symmetric di(p-chlorophenyl)methylene(cyclopentadienyl)(octamethyloctahydrodibenzofluorenyl) zirconium dichloride.

Other references of interest include: US 2016/0244535; US 2017/0362350; WO 2017/034680; WO 2016/53541; WO 2016/53542; WO 2016/114915; U.S. Pat. Nos. 5,382,630; 5,382,631; 8,575,284; 6,069,213; Kim, J D et al., J. Polym. Sci. Part A: Polym. Chem., 38, 1427 (2000); Iedema, P. D. et al., Ind. Eng. Chem. Res., 43, 36 (2004); U.S. Pat. Nos. 6,656,866; 8,815,357; US 2014/0031504; U.S. Pat. Nos. 5,135,526; 7,385,015; WO 2007/080365; WO 2012/006272; US 2014/0242314; WO 00/12565; WO 02/060957; WO 2004/046214; U.S. Pat. Nos. 6,846,770; 6,664,348; US 2005/075525; US 2002/007023; WO 2003/025027; US 2005/0288461; US 2014/0031504; U.S. Pat. Nos. 8,088,867; 5,516,848; 4,701,432; 5,077,255; 7,141,632; 6,207,606; 8,598,061; Polymer Engineering and Science-2007, DOI 10.1002/pen, pages 131-139, published online in Wiley InterScience (www.interscience.wiley.com) 2007 Society of Plastics Engineers; US 2012/0130032; U.S. Pat. Nos. 7,192,902; 8,110,518; 9,193,856; 7,355,058; 9,796,795; US 2018/171040; US 2018/134828; U.S. Pat. No. 9,803,037; U.S. Ser. No. 16/098,592, filed Mar. 31, 2017; Ser. No. 16/266,186, filed Feb. 4, 2019; US 2018/002616; US 2018/002517; US 2017/360237; U.S. Ser. No. 16/315,090, filed Jan. 3, 2019; U.S. Ser. No. 16/315,294, filed Jan. 4, 2019; U.S. Ser.

No. 16/315,722, filed Jan. 7, 2019; U.S. Ser. No. 16/315,874, filed Jan. 7, 2019; and WO 2016/114914.

There is a need for new and improved catalyst systems for the polymerization of propylene-ethylene-diene terpolymers and methods for producing propylene-ethylene-diene terpolymers capable of increased activity while maintaining or improving other polymer properties, as compared to conventional catalyst systems and methods that produce propylene-ethylene-diene terpolymers.

SUMMARY

The present disclosure provides methods for producing an olefin polymer by contacting C_{3+} olefin (such as propylene), ethylene, and diene with a catalyst system including an activator and a catalyst compound represented by formula (I):



wherein:

Cp' is a tetrahydroindacenyl group (such as tetrahydro-s-indacenyl or tetrahydro-as-indacenyl) which is optionally substituted or unsubstituted, provided that when Cp' is tetrahydro-s-indacenyl: 1) the 3 and/or 4 positions are not aryl or substituted aryl, 2) the 3 position is not directly bonded to a group 15 or 16 heteroatom, 3) there are no additional rings fused to the tetrahydroindacenyl ligand, 4) T is not bonded to the 2-position, and 5) the 5, 6, or 7-position (preferably the 6 position) is geminally disubstituted, preferably with two C_1 - C_{10} alkyl groups; M is a group 3, 4, 5, or 6 transition metal, preferably group 4 transition metal, for example titanium, zirconium, or hafnium; T is a bridging group;

y is 0 or 1, indicating the absence or presence of T;

G is a heteroatom group represented by the formula JR_{z-y} where J is N, P, O or S, R' is a C_1 to C_{100} hydrocarbyl group, and z is 2 when J is N or P, and z is 1 when J is O or S; X is a leaving group;

$m=1$; $n=1, 2$ or 3 ; $q=1, 2$ or 3 ; and the sum of $m+n+q$ is equal to the oxidation state of the transition metal (preferably 2, 3, 4, 5, or 6, preferably 4); and obtaining a C_{3+} olefin-ethylene-diene polymer (such as C_3 - C_{40} -olefin-ethylene-diene terpolymer) comprising from 1 to 35 mol % ethylene, from 98.9 to 65 mol % C_{3+} olefin comonomer (such as C_3 to C_{40} comonomer), and from 0.1 to 10 mol % diene.

The present disclosure further provides a polymer obtained by a method of the present disclosure, the polymer having a crystallinity less than 3%; a melt flow rate (at 230° C., 2.16 kg) from less than 100 g/10 min; a glass transition temperature of from -2° C. to -25° C.; and a C_{3+} olefin tacticity ratio [m/r] of greater than 0.4 and less than 1.2; preferably 0.4 to 1.0.

This invention further relates to novel C_{3+} olefin-ethylene-diene polymer (such as C_3 - C_{40} -olefin-ethylene-diene terpolymer) comprising from 1 to 35 mol % ethylene, from 98.9 to 65 mol % C_{3+} olefin (such as C_3 to C_{40} olefin), and from 0.1 to 10 mol % diene, and having a polymer crystallinity of less than 3%; a melt flow rate (at 230° C., 2.16 kg) of less than 100 g/10 minutes; a glass transition temperature of from -2° C. to -25° C.; and a C_{3+} olefin tacticity index ratio [m/r] of greater than 0.4 and less than 1.2; preferably 0.4 to 1.0.

This invention further relates to novel propylene-ethylene-diene polymer comprising from 1 to 35 mol % ethylene, from 98.9 to 65 mol % propylene, and from 0.1 to 10 mol % diene, and having a polymer crystallinity of less than 3%; a melt flow rate (at 230° C., 2.16 kg) of less than 100 g/10

minutes; a glass transition temperature of from -2° C. to -25° C.; and a propylene tacticity index ratio [m/r] of greater than 0.4 and less than 1.2; preferably 0.4 to 1.0.

This invention further relates to novel C_{3+} olefin-ethylene-diene polymer (such as C_3 - C_{40} -olefin-ethylene-diene terpolymer) comprising from 1 to 30 wt % ethylene, from 99-70 wt % C_{3+} olefin (such as C_3 to C_{40} olefin), and from 1 to 21 wt % diene, and having a polymer crystallinity of less than 3%; a melt flow rate (at 230° C., 2.16 kg) of less than 100 g/10 minutes; a glass transition temperature of from -2° C. to -25° C.; and a C_{3+} olefin tacticity index ratio [m/r] from 0.4 to 1.0.

This invention further relates to novel propylene-ethylene-diene polymer comprising from 1 to 30 wt. % ethylene, from 99 to 70 wt. % propylene, and from 1 to 21 wt. % diene, and having a polymer crystallinity of less than 3%; a melt flow rate (at 230° C., 2.16 kg) of less than 100 g/10 minutes; a glass transition temperature of from -2° C. to -25° C.; and a propylene tacticity index ratio [m/r] of greater than 0.4 and less than 1.2; preferably 0.4 to 1.0.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph illustrating catalyst activity of catalysts A and B versus catalyst C at various levels of ENB used in propylene-ENB copolymerizations, according to one embodiment. All catalysts used activator A-1.

FIG. 2 is a graph illustrating catalyst activity for catalyst B versus catalyst C at various levels of ENB used in propylene-ENB copolymerizations, according to one embodiment. Both catalysts used activator A-2.

FIG. 3 is a graph illustrating polymer Mn values at various levels of ENB used in propylene-ENB copolymerizations, according to one embodiment.

DETAILED DESCRIPTION

Definitions

For the purposes of the present disclosure, the numbering scheme for the Periodic Table groups is used as described in CHEMICAL AND ENGINEERING NEWS, 63(5), pg. 27 (1985), e.g., a "group 4 metal" is an element from group 4 of the Periodic Table, e.g. Hf, Ti, or Zr.

An "olefin," alternatively referred to as "alkene," is a linear, branched, or cyclic compound of carbon and hydrogen having at least one carbon-carbon double bond. For purposes of this specification and the claims appended thereto, when a polymer or copolymer is referred to as comprising an olefin, the olefin present in such polymer or copolymer is the polymerized form of the olefin. For example, when a copolymer is said to have an "ethylene" content of 35 wt. % to 55 wt. %, it is understood that the mer unit in the copolymer is derived from ethylene in the polymerization reaction and said derived units are present at 35 wt. % to 55 wt. %, based upon the weight of the copolymer. A "polymer" has two or more of the same or different mer units. A "homopolymer" is a polymer having mer units that are the same. A "copolymer" is a polymer having two or more mer units that are different from each other. A "terpolymer" is a polymer having three or more mer units that are different from each other. "Different" as used to refer to mer units indicates that the mer units differ from each other by at least one atom or are different isomerically. Accordingly, the definition of copolymer, as used herein, includes terpolymers and the like. An "ethylene polymer" or "ethylene copolymer" is a polymer or copolymer comprising

5

at least 50 mol % ethylene derived units, a “propylene polymer” or “propylene copolymer” is a polymer or copolymer comprising at least 50 mol % propylene derived units, and so on.

For the purposes of the present disclosure, ethylene shall be considered an α -olefin.

The terms “hydrocarbyl radical,” “hydrocarbyl” and “hydrocarbyl group” are used interchangeably throughout this document. Likewise the terms “group”, “radical”, and “substituent” are also used interchangeably in this document. For purposes of this disclosure, “hydrocarbyl radical” is defined to be a radical, which contains hydrogen atoms and up to 50 carbon atoms and which may be linear, branched, or cyclic, and when cyclic, aromatic or non-aromatic.

Substituted hydrocarbyl radicals are radicals in which at least one hydrogen atom has been replaced with at least one functional group, such as NR^x , OR^x , SeR^x , TeR^x , PR^x , AsR^x , SbR^x , SR^x , BR^x and the like or where at least one non-hydrocarbon atom or group has been inserted within the hydrocarbyl radical, such as $-\text{O}-$, $-\text{S}-$, $-\text{Se}-$, $-\text{Te}-$, $-\text{N}(\text{R}^x)-$, $=\text{N}-$, $-\text{P}(\text{R}^x)-$, $=\text{P}-$, $-\text{As}(\text{R}^x)-$, $=\text{As}-$, $-\text{Sb}(\text{R}^x)-$, $=\text{Sb}-$, $-\text{B}(\text{R}^x)-$, $=\text{B}-$ and the like, where R^x is independently a hydrocarbyl or halocarbyl radical, and two or more R^x may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure. Examples of substituted hydrocarbyl include $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3$ and $-\text{CH}_2-\text{NMe}_2$ where the radical is bonded via the carbon atom, but would not include groups where the radical is bonded through the heteroatom such as $-\text{OCH}_2\text{CH}_3$ or $-\text{NMe}_2$.

Silylcarbyl radicals are radicals in which one or more hydrocarbyl hydrogen atoms have been substituted with at least one SiR^* containing group or where at least one $-\text{Si}(\text{R}^*)_2-$ has been inserted within the hydrocarbyl radical where R^* is independently a hydrocarbyl or halocarbyl radical, and two or more R^* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure.

Substituted silylcarbyl radicals are radicals in which at least one hydrogen atom has been substituted with at least one functional group such as $-\text{NR}^*$, $-\text{OR}^*$, $-\text{SeR}^*$, $-\text{TeR}^*$, $-\text{PR}^*$, $-\text{AsR}^*$, $-\text{SbR}^*$, $-\text{SR}^*$, $-\text{BR}^*$, $-\text{GeR}^*$, $-\text{SnR}^*$, $-\text{PbR}^*$ and the like or where at least one non-hydrocarbon atom or group has been inserted within the silylcarbyl radical, such as $-\text{O}-$, $-\text{S}-$, $-\text{Se}-$, $-\text{Te}-$, $-\text{N}(\text{R}^*)-$, $=\text{N}-$, $-\text{P}(\text{R}^*)-$, $=\text{P}-$, $-\text{As}(\text{R}^*)-$, $=\text{As}-$, $-\text{Sb}(\text{R}^*)-$, $=\text{Sb}-$, $-\text{B}(\text{R}^*)-$, $=\text{B}-$, $-\text{Ge}(\text{R}^*)_2-$, $-\text{Sn}(\text{R}^*)_2-$, $-\text{Pb}(\text{R}^*)_2-$ and the like, where R^* is independently a hydrocarbyl or halocarbyl radical, and two or more R^* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure. Substituted silylcarbyl radicals are only bonded via a carbon or silicon atom.

Germlylcarbyl radicals are radicals in which one or more hydrocarbyl hydrogen atoms have been substituted with at least one GeR^* containing group or where at least one $-\text{Ge}(\text{R}^*)_2-$ has been inserted within the hydrocarbyl radical where R^* is independently a hydrocarbyl or halocarbyl radical, and two or more R^* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure. Substituted germlylcarbyl radicals are only bonded via a carbon or germanium atom.

6

Substituted germlylcarbyl radicals are radicals in which at least one hydrogen atom has been substituted with at least one functional group such as $-\text{NR}^*$, $-\text{OR}^*$, $-\text{SeR}^*$, $-\text{TeR}^*$, $-\text{PR}^*$, $-\text{AsR}^*$, $-\text{SbR}^*$, $-\text{SR}^*$, $-\text{BR}^*$, $-\text{SiR}^*$, $-\text{SnR}^*$, $-\text{PbR}^*$ and the like or where at least one non-hydrocarbon atom or group has been inserted within the germlylcarbyl radical, such as $-\text{O}-$, $-\text{S}-$, $-\text{Se}-$, $-\text{Te}-$, $-\text{N}(\text{R}^*)-$, $=\text{N}-$, $-\text{P}(\text{R}^*)-$, $=\text{P}-$, $-\text{As}(\text{R}^*)-$, $=\text{As}-$, $-\text{Sb}(\text{R}^*)-$, $=\text{Sb}-$, $-\text{B}(\text{R}^*)-$, $=\text{B}-$, $-\text{Si}(\text{R}^*)_2-$, $-\text{Sn}(\text{R}^*)_2-$, $-\text{Pb}(\text{R}^*)_2-$ and the like, where R^* is independently a hydrocarbyl or halocarbyl radical, and two or more R^* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure.

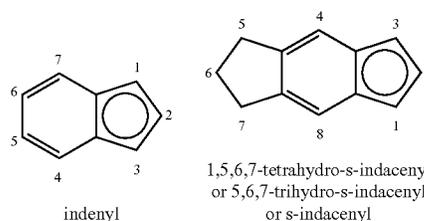
Halocarbyl radicals are radicals in which one or more hydrocarbyl hydrogen atoms have been substituted with at least one halogen (e.g., F, Cl, Br, I) or halogen-containing group (e.g., CF_3).

Substituted halocarbyl radicals are radicals in which at least one halocarbyl hydrogen or halogen atom has been substituted with at least one functional group such as NR^* , OR^* , SeR^* , TeR^* , PR^* , AsR^* , SbR^* , SR^* , BR^* and the like or where at least one non-carbon atom or group has been inserted within the halocarbyl radical such as $-\text{O}-$, $-\text{S}-$, $-\text{Se}-$, $-\text{Te}-$, $-\text{N}(\text{R}^*)-$, $=\text{N}-$, $-\text{P}(\text{R}^*)-$, $=\text{P}-$, $-\text{As}(\text{R}^*)-$, $=\text{As}-$, $-\text{Sb}(\text{R}^*)-$, $=\text{Sb}-$, $-\text{B}(\text{R}^*)-$, $=\text{B}-$ and the like, where R^* is independently a hydrocarbyl or halocarbyl radical provided that at least one halogen atom remains on the original halocarbyl radical. Additionally, two or more R^* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure. Substituted halocarbyl radicals are only bonded via a carbon atom.

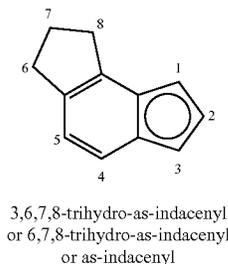
A heteroatom is an atom other than carbon or hydrogen.

The term “aryl” or “aryl group” means a monocyclic or polycyclic aromatic ring and the substituted variants thereof, including phenyl, naphthyl, 2-methyl-phenyl, xylyl, 4-bromo-xylyl. Likewise, “heteroaryl” is an aryl group where a ring carbon atom (or two or three ring carbon atoms) has been replaced with a heteroatom, such as N, O, or S. The term “substituted aryl” means: 1) an aryl group where a hydrogen has been replaced by a substituted or unsubstituted hydrocarbyl group, a substituted or unsubstituted halocarbyl group, a substituted or unsubstituted silylcarbyl group, or a substituted or unsubstituted germlylcarbyl group. The term “substituted heteroaryl” means: 1) a heteroaryl group where a hydrogen has been replaced by a substituted or unsubstituted hydrocarbyl group, a substituted or unsubstituted halocarbyl group, a substituted or unsubstituted silylcarbyl group, or a substituted or unsubstituted germlylcarbyl group.

For nomenclature purposes, the following numbering schemes are used for indenyl, tetrahydro-s-indacenyl and tetrahydro-as-indacenyl ligands.



-continued



As used herein, Mn is number average molecular weight, Mw is weight average molecular weight, and Mz is z average molecular weight, wt. % is weight percent, and mol % is mol percent. Molecular weight distribution (MWD), also referred to as polydispersity, is defined to be Mw divided by Mn. Unless otherwise noted, all molecular weight units (e.g., Mw, Mn, Mz) are g/mol.

The following abbreviations may be used herein: Me is methyl, Et is ethyl, Pr is propyl, cPr is cyclopropyl, nPr is n-propyl, iPr is isopropyl, Bu is butyl, nBu is normal butyl, iBu is isobutyl, sBu is sec-butyl, tBu is tert-butyl, Oct is octyl, Ph is phenyl, Bn is benzyl, Cp is cyclopentadienyl, Ind is indenyl, Flu is fluorenyl, and MAO is methylalumoxane.

For purposes of the present disclosure, a "catalyst system" is the combination of at least one catalyst compound, at least one activator, an optional co-activator, and an optional support material. For the purposes of the present disclosure, when catalyst systems are described as comprising neutral stable forms of the components, it is well understood by one of ordinary skill in the art, that the ionic form of the component is the form that reacts with the monomers to produce polymers. For the purposes of the present disclosure, "catalyst system" includes both neutral and ionic forms of the components of a catalyst system, such as the catalyst compounds.

In the description herein, the catalyst may be described as a catalyst precursor, a pre-catalyst, a pre-catalyst compound, a metallocene catalyst compound, a metallocene catalyst, or a transition metal compound, and these terms are used interchangeably.

A metallocene catalyst is defined as an organometallic transition metal compound with at least one π -bound cyclopentadienyl moiety (or substituted cyclopentadienyl moiety) bound to a transition metal.

For purposes of the present disclosure, in relation to metallocene catalyst compounds, the term "substituted" means that one or more hydrogen atoms have been replaced with a hydrocarbyl, heteroatom (such as a halide), or a heteroatom containing group, (such as silylcarbyl, germylcarbyl, halocarbyl, etc.). For example, methyl cyclopentadiene (Cp) is a Cp group substituted with a methyl group. Two or more adjacent hydrogen atoms may be replaced by a hydrocarbdiyl to form a multi-ring cyclopentadienyl moiety for example, indenyl, fluorenyl, tetrahydro-s-indacenylium and the like.

For purposes of the present disclosure, "alkoxides" include those where the alkyl group is a C_1 to C_{10} hydrocarbyl. The alkyl group may be straight chain, branched, or cyclic. The alkyl group may be saturated or unsaturated. In some embodiments, the alkyl group may comprise at least one aromatic group.

Embodiments

The present disclosure provides methods for producing olefin polymer comprising: i) contacting C_{3+} olefin (such as

C_{3-40} olefin), ethylene, and diene, with a catalyst system comprising activator and a bridged monocyclopentadienyl transition metal compound, and ii) obtaining an C_3 to C_{40} olefin-ethylene-diene terpolymer comprising from 1 to 35 mol % ethylene, from 98.9 to 65 mol % C_3 to C_{40} comonomer, and from 0.1 to 10 mol % diene, wherein the polymer has a crystallinity of less than 3%, a MFR (at 230° C., 2.16 kg) of less than 10 g/10 min, and a Tg of from -2° C. to -25° C. as measured by Differential Scanning calorimetry (DSC). In some embodiments of the present disclosure, the ethylene- C_3 to C_{40} -comonomer-diene polymer has a g' of 0.90 or greater, such as 0.95 or greater, such as 0.98 or greater, such as about 1. Catalyst systems and methods of the present disclosure provide formation of ethylene- C_3 to C_{40} comonomer-diene terpolymers (such as propylene-ethylene-ENB terpolymers) at increased activity levels (e.g., 30,000 gP/mmol cat.hr or greater) and efficiency levels (e.g., 10,000 g poly/g cat or greater) while maintaining or improving other polymer properties (such as Mn), as compared to conventional catalyst systems and methods that produce propylene-ethylene-diene terpolymers.

Olefin-Ethylene-Diene Polymer

The present disclosure provides compositions of matter produced by the methods of the present disclosure.

The term "olefin-ethylene-diene polymer" as used herein can be any polymer comprising C_{3+} olefin (such as C_3 - C_{40} monomer, preferably propylene), ethylene, and a diene. Preferably, the olefin-ethylene-diene polymer is an α -olefin-ethylene-diene polymer. Preferably, the α -olefin-ethylene-diene polymer is a terpolymer and includes α -olefin-derived units, ethylene-derived units, and diene-derived units. For example, the α -olefin-ethylene-diene terpolymer may be a propylene-ethylene-diene terpolymer (PEDM). The propylene-ethylene-diene terpolymers may be prepared by polymerizing ethylene and propylene with one or more dienes.

A C_3 to C_{40} monomer can be a C_3 - C_{40} α -olefin. C_3 - C_{40} α -olefins include substituted or unsubstituted C_3 to C_{40} α -olefins, such as C_3 to C_{20} α -olefins, such as C_3 to C_{12} α -olefins, preferably propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene and isomers thereof. C_3 to C_{40} α -olefins may be linear, branched, or cyclic. C_3 to C_{40} cyclic olefins may be strained or unstrained, monocyclic or polycyclic, and may include heteroatoms and/or one or more functional groups. Non-limiting examples of cyclic olefins include norbornene, cyclopentene, 5-methylcyclopentene, cycloheptene, cyclooctene, and cyclododecene. Preferred linear α -olefins include propylene, 1-butene, 1-hexene, or 1-octene. Preferred branched C_3 - C_{40} α -olefins include 4-methyl-1-pentene, 3-methyl-1-pentene, 5-methyl-1-nonene, and 3,5,5-trimethyl-1-hexene. Preferred α -olefin comonomers are propylene and 1-butene, most preferably propylene.

Dienes may be conjugated or non-conjugated, acyclic or cyclic. Preferably, the dienes are non-conjugated. Dienes can include 5-ethylidene-2-norbornene (ENB); 5-vinyl-2-norbornene (VNB); 1,4-hexadiene; 5-methylene-2-norbornene (MNB); 1,6-octadiene; 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene (MOD); 1,3-cyclopentadiene; 1,4-cyclohexadiene; dicyclopentadiene (DCPD); and combinations thereof. Other exemplary dienes include butadiene, pentadiene, hexadiene, heptadiene, octadiene, nonadiene, decadiene, undecadiene, dodecadiene, tridecadiene, tetradecadiene, pentadecadiene, hexadecadiene, heptadecadiene, octadecadiene, nonadecadiene, icosadiene, heneicosadiene, docosadiene, tricosadiene, tetracosadiene, pentacosadiene, hexacosadiene, heptacosadiene, octacosadiene, nonacosadiene, triacontadiene, and isomers thereof.

Examples of α,ω -dienes include 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, 1,13-tetradecadiene. Low molecular weight polybutadienes (Mw less than 1000 g/mol) may also be used as the diene, which is sometimes also referred to as a polyene. Cyclic dienes include cyclopentadiene, norbornadiene, 5-ethylidene-2-norbornene, 5-vinyl-2-norbornene, divinylbenzene, dicyclopentadiene or higher ring containing diolefins with or without substituents at various ring positions.

In some embodiments the diene is preferably 5-ethylidene-2-norbornene; 1,4-hexadiene; 5-methylene-2-norbornene; 1,6-octadiene; 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; dicyclopentadiene; and combinations thereof. Preferably, the diene is 5-ethylidene-2-norbornene.

Typically, the α -olefin-ethylene-diene polymer has an α -olefin content of from 98.9 mol % to 65 mol %, such as from 98.5 to 77 mol %, such as from 98 mol % to 70 mol %, such as from 95 mol % to 75 mol %, such as from 95 mol % to 80 mol %, such as from 95 mol % to 85 mol %. Preferably, the α -olefin content is from 98.9 to 65 mol %, such as from 95 mol % to 70 mol %, such as from 95 mol % to 75 mol %. In some embodiments of the invention, the α -olefin content is greater than 77 mol %, such as greater than 80 mol %, such as greater than 85 mol % such as greater than 90 mol %, with an upper limit of 98.9 mol % or less, such as 98 mol % or less, such as 97 mol % or less, such as 96 mol % or less, such as 95 mol % or less. The balance of the α -olefin-ethylene-diene polymer comprises ethylene and one or more dienes.

The α -olefin-ethylene-diene polymer has an ethylene content of from 0.1 mol % to 35 mol %, such as from 0.5 to 30 mol %, such as from 1 mol % to 25 mol %, such as from 1 mol % to 22 mol %, such as from 2 mol % to 20 mol %, such as from 5 mol % to 20 mol %, such as from 5 mol % to 10 mol %. In some embodiments of the invention, the ethylene content is less than 22 mol %, such as less than 20 mol %, such as less than 18 mol %, with a lower limit of 1 mol % or greater, such as 2 mol % or greater, such as 5 mol % of greater. The balance of the α -olefin-ethylene-diene polymer comprises one or more α -olefins and one or more dienes.

In embodiments of the invention, the α -olefin-ethylene-diene polymer has a diene content of from 0.1 mol % to 10 mol %, such as from 0.2 mol % to 9 mol %, such as from 0.5 mol % to 8 mol %, such as from 0.5 mol % to 7 mol %, such as from 0.5 mol % to 6 mol %, such as from 0.6 mol % to 5 mol %. Other preferred ranges can include from 1 mol % to 10 mol %, such as from 1 mol % to 5 mol %, such as from 1 mol % to 4 mol %, such as from 1 mol % to 3 mol %. In some embodiments of the invention, the α -olefin-ethylene-diene polymer has a diene content is 0.5 mol % or greater and 10 mol % or less.

In one or more embodiments of the invention, the α -olefin-ethylene-diene polymer may comprise 5-ethylidene-2-norbornene in an amount of from 0.1 mol % to 10 mol %, such as from 0.2 mol % to 9 mol %, such as from 0.5 mol % to 8 mol %, such as from 0.5 mol % to 7 mol %, or from 0.5 mol % to 6 mol %, such as from 0.6 mol % to 5 mol %. The balance of the α -olefin-ethylene-diene polymer comprises one or more α -olefins and ethylene. In some embodiments of the invention, the α -olefin-ethylene-diene polymer has a 5-ethylidene-2-norbornene content is 0.5 mol % or greater and 10 mol % or less.

In alternate embodiments, the α -olefin-ethylene-diene polymer is a propylene-ethylene-diene terpolymer having an ethylene content from 1 wt % to 30 wt % (such as from 2 wt % to 20 wt %), a propylene content from 70 wt % to 98 wt % (such as from 75 wt % to 95 wt %), and from 1 to 21 wt % diene.

In another embodiment of the invention, the propylene-ethylene-diene terpolymer may have an ethylene amount of from 2 wt % by weight to 25 wt % by weight, or from 5 wt % by weight to 25 wt % by weight, or from 10 wt % by weight to 25 wt % by weight, or from 15 wt % by weight to 25 wt % by weight, or from 20 wt % by weight to 25 wt % by weight, or from 5 wt % by weight to 10 wt % by weight, or from 10 wt % by weight to 20 wt % by weight, or from 15 wt % by weight to 20 wt % by weight based on the weight of the polymer. The balance of the propylene-ethylene-diene terpolymer comprises propylene and, one or more dienes.

Preferably, the propylene-ethylene-diene terpolymer comprises a diene content of from 1 wt % by weight to 21 wt % by weight based on the weight of the polymer, or from 1.5 wt % by weight to 15 wt % by weight, or from 2 wt % by weight to 15 wt % by weight, or from 3 wt % by weight to 10 wt % by weight, or from 4 wt % by weight to 8 wt % by weight. Other preferred ranges may include from 1 wt % by weight to 18 wt % by weight, or from 1 wt % by weight to 15 wt % by weight, or from 1 wt % by weight to 10 wt % by weight, or from 10 wt % by weight to 21 wt % by weight, or from 3 wt % by weight to 12 wt % by weight, or from 5 wt % by weight to 12 wt % by weight based on the weight of the polymer. In one or more embodiments of the invention, the propylene-ethylene-diene terpolymer comprises 5-ethylidene-2-norbornene (ENB).

The α -olefin-ethylene-diene polymer may have a weight average molecular weight (Mw) of 5,000,000 g/mol or less, a number average molecular weight (Mn) of 3,000,000 g/mol or less, a z-average molecular weight (Mz) of 10,000,000 g/mol or less, and, optionally, a g' index of 0.90 or greater, all of which may be determined by size exclusion chromatography.

For purposes of the present disclosure, the mole fractions of ethylene, C₃-C₄₀ olefin, and diene are calculated using the following equations A, B, and C, respectively:

C₂ mole fraction = Equation (A)

$$\frac{\frac{\text{wt. \% } C_2}{\text{Mw}(C_2)}}{\frac{\text{wt. \% } C_2}{\text{Mw}(C_2)} + \frac{100 - \text{wt. \% } C_2 - \text{wt. \% diene}}{\text{Mw}(C_3 - C_{40} \text{ olefin})} + \frac{\text{wt. \% diene}}{\text{Mw}(\text{diene})}}$$

C₃ - C₄₀ mole fraction = Equation (B)

$$\frac{\frac{100 - \text{wt. \% } C_2 - \text{wt. \% diene}}{\text{Mw}(C_3 - C_{40} \text{ olefin})}}{\frac{\text{wt. \% } C_2}{\text{Mw}(C_2)} + \frac{100 - \text{wt. \% } C_2 - \text{wt. \% diene}}{\text{Mw}(C_3 - C_{40} \text{ olefin})} + \frac{\text{wt. \% diene}}{\text{Mw}(\text{diene})}}$$

-continued

Diene mole fraction =

$$\frac{\text{wt. \% diene}}{\text{Mw}(\text{diene})} \div \left(\frac{\text{wt. \% C}_2}{\text{Mw}(\text{C}_2)} + \frac{100 - \text{wt. \% C}_2 - \text{wt. \% diene}}{\text{Mw}(\text{C}_3 - \text{C}_{40} \text{ olefin})} + \frac{\text{wt. \% diene}}{\text{Mw}(\text{diene})} \right)$$

where “Mw(C₂)” is the molecular weight of ethylene in g/mol, “Mw(C₃-C₄₀ olefin)” is the molecular weight of the C₃-C₄₀ olefin in g/mol, and “Mw(diene)” is the molecular weight of diene in g/mol.

Wt. % of C₂, wt. % of C₃-C₄₀ olefin and wt. % of diene can be measured by ¹³C NMR and in some cases by ¹H NMR. Wt. % numbers throughout this document are corrected numbers wherein wt. % of C₂ plus wt. % of C₃-C₄₀ olefin plus wt. % of diene equals 100%, unless specifically referred to as being uncorrected. Uncorrected values ignore the diene component of the polymer (i.e. wt. % of C₂ plus wt. % of C₃-C₄₀ olefin equals 100%).

For ethylene-propylene and ethylene-propylene-diene copolymers, FTIR is typically used to measure ethylene and diene content (when present), using ASTM D3900 and ASTM D6047. The former provides uncorrected C₂ wt. % values.

The wt. % of C₂ can be calculated from uncorrected wt. % C₂ using the equation below:

$$\text{wt. \% C}_2 = [\text{uncorrected wt. \% C}_2 \times (100 - \text{wt. \% diene})] / 100$$

where the wt. % of ethylene and wt. % of diene are determined by FTIR or by NMR methods.

When the C₃-C₄₀ olefin is propylene, ASTM D3900 is followed to determine propylene content. When the diene is ENB, ASTM D6047 is followed to determine ENB content. If ASTM established IR methods are not available for other C₃-C₄₀ olefins, and/or other dienes, ¹³C NMR may be used (in event of conflict between FTIR and ¹³C NMR, the ¹³C NMR shall be used).

The mole percents (mol %) of ethylene, C₃-C₄₀ olefin, and diene are then calculated by multiplying mole fraction of ethylene, C₃-C₄₀ olefin, and diene, respectively, by 100.

The α-olefin-ethylene-diene polymer of the present disclosure may have an Mn of from 5,000 to 500,000 g/mol, such as from 10,000 to 400,000 g/mol, such as from 20,000 to 300,000 g/mol, such as from 40,000 to 250,000 g/mol, such as from 50,000 to 200,000 g/mol. The α-olefin-ethylene-diene polymer of the present disclosure may have an Mw of from 5,000 to 1,000,000 g/mol, such as from 20,000 to 800,000 g/mol, such as from 50,000 to 700,000 g/mol, such as from 50,000 to 500,000 g/mol, such as from 90,000 to 450,000 g/mol. The α-olefin-ethylene-diene polymer of the present disclosure may have an Mz of from 5,000 to 1,500,000 g/mol, such as from 100,000 to 1,000,000 g/mol, such as from 150,000 to 800,000 g/mol, such as from 170,000 to 750,000 g/mol. For purposes of this disclosure, the Mw, Mn and Mz will be defined as measured by an IR detector (GPC-IR).

The molecular weight distribution (MWD=(Mw/Mn)), also referred to as a “polydispersity index” (PDI), of the α-olefin-ethylene-diene polymer may be from 1.2 to 40. For example, an α-olefin-ethylene-diene polymer may have an MWD with an upper limit of 40, or 30, or 20, or 10, or 9, or 8, or 7, or 6, or 5, or 4, or 3, and a lower limit of 1.2, or 1.3, or 1.4, or 1.5, or 1.6, or 1.7, or 1.8, or 2.0. In one or more embodiments, the MWD of the α-olefin-ethylene-diene

Equation (C)

polymer is from 1 to 10, such as from 1.2 to 7, such as from 1.5 to 5, such as from 1.8 to 3. In one or more embodiments, the MWD of the α-olefin-ethylene-diene polymer is greater than 1.8 and less than 4.5. For purposes of this disclosure, the PDI will be defined as the Mw/Mn as measured by an IR detector (GPC-IR).

The α-olefin-ethylene-diene polymer of the present disclosure may have a g' index value of 0.90 or greater, such as at least 0.95, or at least 0.98, or at least 0.99, wherein g' is measured at the Mw of the polymer using the intrinsic viscosity of isotactic polypropylene as the baseline. For use herein, the branching index, g' (also referred to as g' index or g'vis), is defined as:

$$g' = \frac{\eta_b}{\eta_l}$$

where η_b is the intrinsic viscosity of the α-olefin-ethylene-diene polymer and η_l is the intrinsic viscosity of a linear polymer of the same viscosity-averaged molecular weight (M_v) as the α-olefin-ethylene-diene polymer. Thus, η_l=Kw_v^α, where K and α are as described below in the GPC-SEC method herein for determining molecular weights.

In another embodiment of the invention, the α-olefin-ethylene-diene polymer may have a g' index value of from 0.80 to less than 0.95, indicating a polymer structure with a small amount of long chain branching.

The α-olefin-ethylene-diene polymer of the present disclosure may have a density of from 0.83 g/cm³ to 0.92 g/cm³, or from 0.85 g/cm³ to 0.91 g/cm³, or from 0.85 g/cm³ to 0.90 g/cm³, at room temperature as determined by ASTM D-1505 test method.

The α-olefin-ethylene-diene polymer of the present disclosure may have a melt flow rate (MFR, 2.16 kg weight at 230° C.), equal to or greater than 0.2 g/10 min as measured according to ASTM D-1238. Preferably, the MFR (2.16 kg at 230° C.) is from 0.2 g/10 min to 200 g/10 min, such as from 0.2 g/10 min to 100 g/10 min, such as from 0.2 g/10 min to 60 g/10 min, such as from 0.2 g/10 min to 50 g/10 min, such as from 0.2 g/10 min to 30 g/10 min, such as from 0.2 g/10 min to 25 g/10 min, such as from 0.5 g/10 min to 25 g/10 min, such as from 0.5 g/10 min to 10 g/10 min. In some embodiments of the invention, the MFR is less than 100 g/10 min, alternatively less than 80 g/10 min, alternatively less than 60 g/10 min, alternatively less than 40 g/10 min, alternatively less than 20 g/10 min, alternatively less than 10 g/10 min. In some embodiments of the invention, the MFR is less than 20 g/10 min, preferably less than 10 g/10 min.

The α-olefin-ethylene-diene polymer of the present disclosure may have a Mooney viscosity ML (1+4) at 125° C., as determined according to ASTM D1646, of greater than 5, or greater than 10, or greater than 15, or greater than 20.

The α-olefin-ethylene-diene polymer of the present disclosure may have a heat of fusion (H_f) determined by the

Keii and K. Soga, Eds. (Elsevier, 1986), pp. 271-292; and 2) U.S. Patent Application Publication No. US2004/054086 (paragraphs [0043] to [0054]).

Similarly *m* diads and *r* diads can be calculated as follows where *mm*, *mr* and *mr* are defined above:

$$m = mm + \frac{1}{2} mr$$

$$r = rr + \frac{1}{2} mr$$

Preferably, the “propylene tacticity index” [*m/r*] of an α -olefin-ethylene-diene polymer of the present disclosure is greater than 0.40, alternatively greater than 0.50, alternatively greater than 0.55, alternatively greater than 0.60 and with an upper limit of 1.2, alternatively 1.1, alternatively, 1.0, alternatively 0.9.

Analogous calculations can be done for other C_{3+} olefin polymers including those with a low content of ethylene. For further information see J. C. Randall, Polymer Reviews, “A Review of High Resolution liquid ^{13}C NMR Characterizations of ethylene-based polymers” (1989) 29:2 201-317.

In a preferred embodiment the polymer produced herein has a unimodal or multimodal molecular weight distribution as determined by Gel Permeation Chromatography (GPC). By “unimodal” is meant that the GPC trace has one peak or inflection point. By “multimodal” is meant that the GPC trace has at least two peaks or inflection points. An inflection point is that point where the second derivative of the curve changes in sign (e.g., from negative to positive or vice versus).

Unless otherwise indicated *M_w*, *M_n* and *M_w/M_n* are determined by using High Temperature Gel Permeation Chromatography as described in the Experimental section below.

In a preferred embodiment the polymer produced herein has a composition distribution breadth index (CDBI) of 50% or more, preferably 60% or more, preferably 70% or more. CDBI is a measure of the composition distribution of monomer within the polymer chains and is measured by the procedure described in PCT publication WO 93/03093, published Feb. 18, 1993, specifically columns 7 and 8 as well as in Wild et al, J. Poly. Sci., Poly. Phys. Ed., Vol. 20, p. 441 (1982) and U.S. Pat. No. 5,008,204, including that fractions having a weight average molecular weight (*M_w*) below 15,000 are ignored when determining CDBI.

The α -olefin-ethylene-diene polymer of the present disclosure may be a blend of discrete α -olefin-ethylene-diene polymers as long as the polymer blend has the properties of the α -olefin-ethylene-diene terpolymer as described herein. The number of α -olefin-ethylene-diene polymers may be three or less, or two or less. In one or more embodiments, the α -olefin-ethylene-diene polymer includes a blend of two α -olefin-ethylene-diene terpolymers differing in the ethylene content, and/or the alpha-olefin content, and/or the diene content. In one or more embodiments, the α -olefin-ethylene-diene polymer includes a blend of two propylene-ethylene-diene terpolymers differing in the ethylene content, and/or the propylene content, and/or the diene content. In one or more embodiments, an α -olefin-ethylene-diene polymer includes a blend of two butene-ethylene-diene terpolymers differing in the ethylene content, and/or the butene content, and/or the diene content. Preparation of such polymer blends may be as described in US 2004/0024146 and US 2006/0183861.

Compositions comprising the α -olefin-ethylene-diene polymer may contain the α -olefin-ethylene-diene polymer in an amount of from 5 wt % to 99 wt %, such as from 5 wt % to 30 wt %, based on the weight of the composition.

Preferably, the composition includes the α -olefin-ethylene-diene polymer in an amount of from 5 wt % to 95 wt %, such as from 10 wt % to 90 wt %, such as from 15 wt % to 80 wt %, such as from 20 wt % to 75 wt %, such as from 25 wt % to 70 wt %, such as from 30 wt % to 65 wt %, such as from 35 wt % to 60 wt %, such as from 40 wt % to 50 wt %, based on the weight of the composition. Compositions may be tire tread compositions and/or adhesive blend compositions. Blends

In another embodiment, the α -olefin-ethylene-diene polymer produced herein is combined with one or more additional polymers prior to being formed into a film, molded part or other article. Other useful polymers include polyethylene, isotactic polypropylene, highly isotactic polypropylene, syndiotactic polypropylene, random copolymer of propylene and ethylene, and/or butene, and/or hexene, polybutene, ethylene vinyl acetate, LDPE, LLDPE, HDPE, ethylene vinyl acetate, ethylene methyl acrylate, copolymers of acrylic acid, polymethylmethacrylate or any other polymers polymerizable by a high-pressure free radical process, polyvinylchloride, polybutene-1, isotactic polybutene, ABS resins, ethylene-propylene rubber (EPR), vulcanized EPR, EPDM, block copolymer, styrenic block copolymers, polyamides, polycarbonates, PET resins, cross linked polyethylene, copolymers of ethylene and vinyl alcohol (EVOH), polymers of aromatic monomers such as polystyrene, poly-1 esters, polyacetal, polyvinylidene fluoride, polyethylene glycols, polyisobutylene and/or thermoplastic vulcanizate compositions.

In at least one embodiment, the α -olefin-ethylene-diene polymer is present in the above blends, at from 10 to 99 wt %, based upon the weight of the polymers in the blend, preferably 20 to 95 wt %, even more preferably at least 30 to 90 wt %, even more preferably at least 40 to 90 wt %, even more preferably at least 50 to 90 wt %, even more preferably at least 60 to 90 wt %, even more preferably at least 70 to 90 wt %.

Additionally, additives may be included in the blend, in one or more components of the blend, and/or in a product formed from the blend, such as a film, as desired. Such additives are well known in the art, and can include, for example: fillers; antioxidants (e.g., hindered phenolics such as IRGANOX™ 1010 or IRGANOX™ 1076 available from Ciba-Geigy); phosphites (e.g., IRGAFOS™ 168 available from Ciba-Geigy); anti-cling additives; tackifiers, such as polybutenes, terpene resins, aliphatic and aromatic hydrocarbon resins, alkali metal and glycerol stearates, and hydrogenated rosins; UV stabilizers; heat stabilizers; anti-blocking agents; release agents; anti-static agents; pigments; colorants; dyes; waxes; silica; fillers; talc; and the like. Films

The α -olefin-ethylene-diene polymer of the present disclosure, or blends/compositions thereof, may be used in a variety of end-use applications. Such applications include, for example, mono- or multi-layer blown, extruded, and/or shrink films. These films may be formed by any number of well-known extrusion or coextrusion techniques, such as a blown bubble film processing technique, wherein the composition can be extruded in a molten state through an annular die and then expanded to form a uni-axial or biaxial orientation melt prior to being cooled to form a tubular, blown film, which can then be axially slit and unfolded to form a flat film. Films may be subsequently unoriented, uniaxially oriented, or biaxially oriented to the same or different extents. One or more of the layers of the film may be oriented in the transverse and/or longitudinal directions to the same or different extents. The uniaxially orientation can

be accomplished using typical cold drawing or hot drawing methods. Biaxial orientation can be accomplished using tenter frame equipment or a double bubble processes and may occur before or after the individual layers are brought together. For example, a polyethylene layer can be extrusion coated or laminated onto an oriented polypropylene layer or the polyethylene and polypropylene can be coextruded together into a film then oriented. Likewise, oriented polypropylene could be laminated to oriented polyethylene or oriented polyethylene could be coated onto polypropylene then optionally the combination could be oriented even further. Typically the films are oriented in the Machine Direction (MD) at a ratio of up to 15, preferably between 5 and 7, and in the Transverse Direction (TD) at a ratio of up to 15, preferably 7 to 9. However, in another embodiment the film is oriented to the same extent in both the MD and TD directions.

The films may vary in thickness depending on the intended application; however, films of a thickness from 1 to 50 μm are usually suitable. Films intended for packaging are usually from 10 to 50 μm thick. The thickness of the sealing layer is typically 0.2 to 50 μm . There may be a sealing layer on both the inner and outer surfaces of the film or the sealing layer may be present on only the inner or the outer surface.

In another embodiment, one or more layers may be modified by corona treatment, electron beam irradiation, gamma irradiation, flame treatment, or microwave. In at least one embodiment, one or both of the surface layers is modified by corona treatment.

Uses

The α -olefin-ethylene-diene polymers of the present disclosure may be used as a blend component in rubber containing articles such as tires (sidewall and/or tread), hoses, weather seals, and belts. Because of the higher propylene tacticity index indicating a more atactic like polymer structure, applications requiring tackiness are well suited. The α -olefin-ethylene-diene polymers are also useful as components in adhesives and bonding agents.

In preferred embodiments of the invention the polymer prepared herein may be used in a tire sidewall, a retreaded tire, a truck tire, an off-road tire, a passenger automobile tire, a bus tire, a motorcycle tire, a bicycle tire, or an aircraft tire.

In preferred embodiments of the invention the polymer prepared herein may be used in a tire tread, an adhesive composition, a rubber composition, a belt, a thermoplastic vulcanizate composition, a vibration damping device, and or a bonding agent.

Polymerization Processes

The present disclosure provides polymerization processes including contacting ethylene, $\text{C}_3\text{-C}_{40}$ comonomer, such as a $\text{C}_3\text{-C}_{40}$ α -olefin (such as propylene), and diene (such as ENB) with a catalyst system comprising an activator, optional support, and a catalyst compound. The catalyst compound, optional support and activator may be combined in any order, and are combined typically prior to contacting the catalyst system with the monomers (ethylene, $\text{C}_3\text{-C}_{40}$ comonomer, and diene).

Useful C_3 to C_{40} comonomers include $\text{C}_3\text{-C}_{40}$ α -olefins. $\text{C}_3\text{-C}_{40}$ α -olefins include substituted or unsubstituted C_3 to C_{40} α -olefins, such as C_3 to C_{20} α -olefins, such as C_3 to C_{12} α -olefins, preferably propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene and isomers thereof. C_3 to C_{40} α -olefins may be linear, branched, or cyclic. C_3 to C_{40} cyclic olefins may be strained or unstrained, monocyclic or polycyclic, and may include heteroatoms and/or one or more functional groups. Non-limiting examples of cyclic olefins include norbornene,

cyclopentene, 5-methylcyclopentene, cycloheptene, cyclooctene, and cyclododecene. Preferred linear α -olefins include propylene, 1-butene, 1-hexene, or 1-octene. Preferred branched $\text{C}_3\text{-C}_{40}$ α -olefins include 4-methyl-1-pentene, 3-methyl-1-pentene, 5-methyl-1-nonene, and 3,5,5-trimethyl-1-hexene. Preferred α -olefin comonomers are propylene and 1-butene, most preferably propylene.

Dienes may be conjugated or non-conjugated, acyclic or cyclic. Preferably, the dienes are non-conjugated. Dienes can include 5-ethylidene-2-norbornene (ENB); 5-vinyl-2-norbornene (VNB); 1,4-hexadiene; 5-methylene-2-norbornene (MNB); 1,6-octadiene; 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene (MOD); 1,3-cyclopentadiene; 1,4-cyclohexadiene; dicyclopentadiene (DCPD); and combinations thereof. Other exemplary dienes include butadiene, pentadiene, hexadiene, heptadiene, octadiene, nonadiene, decadiene, undecadiene, dodecadiene, tridecadiene, tetradecadiene, pentadecadiene, hexadecadiene, heptadecadiene, octadecadiene, nonadecadiene, icosadiene, heneicosadiene, docosadiene, tricosadiene, tetracosadiene, pentacosadiene, hexacosadiene, heptacosadiene, octacosadiene, nonacosadiene, triacontadiene, and isomers thereof. Examples of α,ω -dienes include 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, 1,13-tetradecadiene. Low molecular weight polybutadienes (Mw less than 1000 g/mol) may also be used as the diene, which is sometimes also referred to as a polyene. Cyclic dienes include cyclopentadiene, vinylnorbornene, norbornadiene, 5-ethylidene-2-norbornene, 5-vinyl-2-norbornene, divinylbenzene, dicyclopentadiene or higher ring containing diolefins with or without substituents at various ring positions. Preferably, the diene is ENB.

In at least one embodiment, one or more dienes are present in the polymer produced herein at up to 25 weight %, such as from 0.00001 wt % to 21 wt %, such as from 0.1 wt % to 15 wt %, such as from 0.5 to 10 wt %, such as from 1 to 8 wt %, such as from 1 to 5 wt %, such as from 1 to 3 wt % based upon the total weight of the composition. In some embodiments 50,000 ppm or less of diene is added to a polymerization, such as from 50 ppm to 500 ppm, such as from 100 ppm to 400 ppm, such as from 200 ppm to 300 ppm. In at least one embodiment, a diene is introduced into a polymerization reactor at a rate of 0.1 g/min to 10 g/min, such as from 0.2 g/min to 5 g/min, such as from 0.2 g/min to 1 g/min, such as from 0.2 g/min to 0.5 g/min, such as from 0.3 g/min to 0.4 g/min.

Polymerization processes of the present disclosure can be carried out in any suitable manner, such as any suitable suspension, homogeneous, bulk, solution, slurry, or gas phase polymerization process. Such processes can be run in a batch, semi-batch, or continuous mode. Gas phase polymerization processes and slurry processes are preferred.

A homogeneous polymerization process is a process where at least 90 wt % of the product is soluble in the reaction media. A bulk polymerization is a polymerization process in which the monomers and/or comonomers being polymerized are used as a solvent or diluent using little or no inert solvent as a solvent or diluent. A small fraction of inert solvent might be used as a carrier for catalyst and scavenger. A bulk polymerization system preferably contains less than 25 wt % of inert solvent or diluent, preferably less than 10 wt %, preferably less than 1 wt %, preferably 0 wt %. Alternatively, no solvent or diluent is present or added in the reaction medium, (except for the small amounts used as the

carrier for the catalyst system or other additives, or amounts typically found with the monomer; e.g., propane in propylene).

In another embodiment, the process is a slurry process. As used herein the term "slurry polymerization process" includes a polymerization process where a supported catalyst is used and monomers are polymerized on or around the supported catalyst particles. Typically, at least 95 wt % of polymer products obtained from the supported catalyst after polymerization are in granular form as solid particles (not dissolved in the diluent).

Suitable diluents/solvents for polymerization include non-coordinating, inert liquids. Examples include straight and branched-chain hydrocarbons, such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof, such as can be found commercially (Isopar™, which is isoparaffins); perhalogenated hydrocarbons, such as perfluorinated C₄₋₁₀ alkanes, chlorobenzene, and aromatic and alkylsubstituted aromatic compounds, such as benzene, toluene, mesitylene, and xylene. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, 1-butene, 1-hexene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-octene, 1-decene, and mixtures thereof. In at least one embodiment, aliphatic hydrocarbon solvents are used as the solvent, such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof. In another embodiment, the solvent is not aromatic, preferably aromatics are present in the solvent at less than 1 wt %, preferably less than 0.5 wt %, preferably 0 wt % based upon the weight of the solvents.

In at least one embodiment, the feed concentration of the monomers and comonomers for the polymerization is from 1 vol % in solvent to 60 vol % in solvent, such as 1 vol % in solvent to 40 vol % in solvent, such as 1 vol % in solvent to 20 vol % in solvent, based on the total volume of the feedstream. Preferably the polymerization is a continuous process.

Preferred polymerizations can be run at any temperature and/or pressure suitable to obtain the desired polymers. Typical temperatures and/or pressures include a temperature in the range of from 0° C. to 300° C., such as 20° C. to 200° C., such as 40° C. to 180° C., such as from 50° C. to 160° C., such as from 60° C. to 140° C.; and at a pressure from 0.35 MPa to 16 MPa, such as from 0.45 MPa to 13 MPa, such as from 0.5 MPa to 12 MPa, such as from 2 MPa to 10 MPa, for example 2.2 MPa. In some embodiments of the invention, the pressure is from 0.35 MPa to 17.23 MPa.

In a typical polymerization, the run time of the reaction is up to 300 minutes, preferably in the range of from about 5 to 250 minutes, or preferably from about 10 to 120 minutes.

In some embodiments hydrogen is present in the polymerization reactor at a partial pressure of 0.001 to 50 psig (0.007 to 345 kPa), preferably from 0.01 to 25 psig (0.07 to 172 kPa), more preferably 0.1 to 10 psig (0.7 to 70 kPa).

In at least one embodiment, the catalyst efficiency is from 5,000 g polymer/g catalyst (g poly/g cat) to 1,000,000 g poly/g cat, such as from 10,000 g poly/g cat to 500,000 g poly/g cat, such as from 10,000 g poly/g cat to 250,000 g poly/g cat, such as from 11,000 g poly/g cat to 200,000 g poly/g cat, such as from 11,000 g poly/g cat to 50,000 g poly/g cat. In another embodiment, the catalyst efficiency is

greater than 10,000 g poly/g cat, alternatively greater than 15,000 g poly/g cat, alternatively greater than 20,000 g poly/g cat, alternatively greater than 25,000 g poly/g cat, alternatively greater than 30,000 g poly/g cat, alternatively greater than 40,000 g poly/g cat, alternatively greater than 50,000 g poly/g cat, alternatively greater than 75,000 g poly/g cat, alternatively greater than 100,000 g poly/g cat, alternatively greater than 150,000 g poly/g cat, alternatively greater than 200,000 g poly/g cat, alternatively greater than 250,000 g poly/g cat.

For calculating catalyst efficiency, also referred to as catalyst productivity, only the weight of the transition metal component of the catalyst is used.

In at least one embodiment, little or no scavenger is used in the process to produce the polymer. In some embodiments, scavenger (such as trialkyl aluminum) is present at zero mol %, alternately the scavenger is present at a molar ratio of scavenger metal to transition metal of less than 100:1, preferably less than 50:1, preferably less than 30:1.

In some embodiments of the invention, the polymerization: 1) is conducted at temperatures of 0° C. to 300° C. (such as 25° C. to 200° C., such as 40° C. to 180° C., such as 50° C. to 160° C., such as 60° C. to 140° C., such as 60° C. to 130° C., such as 60° C. to 120° C.); 2) is conducted at a pressure of atmospheric pressure from to 25 MPa (such as 1 to 20 MPa, such as from 1 to 15 MPa, such as 2 to 14 MPa, such as 2 to 13 MPa, such as 2 to 12 MPa, such as 2 to 11 MPa, such as 2 to 10 MPa); 3) is conducted in an aliphatic hydrocarbon solvent (such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; preferably where aromatics are preferably present in the solvent at less than 1 wt %, preferably less than 0.5 wt %, preferably at 0 wt % based upon the weight of the solvents); 4) the polymerization can occur in one reaction zone; and 5) optionally hydrogen is present in the polymerization reactor at a wt-ppm hydrogen to ethylene of 0 to 1000 wt ppm, alternatively 0 to 800 wt ppm, alternatively 0 to 600 ppm, alternatively 0 to 500 ppm, alternatively 0 to 400 ppm, alternatively 0 to 300 ppm, alternatively 0 to 200 ppm, alternatively 0 to 150 ppm, alternatively 0 to 100 ppm. In some embodiments hydrogen is present in the polymerization reactor at a wt-pp hydrogen to ethylene of less than 1000 wt ppm, alternatively, less than 750 ppm, alternatively less than 500 ppm, alternatively less than 400 ppm, alternatively less than 300 ppm, alternatively less than 300 ppm, alternatively less than 200 ppm, alternatively less than 150 ppm, alternatively less than 100 ppm, alternatively less than 50 ppm.

A "reaction zone" also referred to as a "polymerization zone" is a vessel where polymerization takes place, for example a batch or continuous reactor. When multiple reactors are used in either series or parallel configuration, each reactor is considered as a separate polymerization zone. For a multi-stage polymerization in both a batch reactor and a continuous reactor, each polymerization stage is considered as a separate polymerization zone. In at least one embodiment, the polymerization occurs in one reaction zone. In an alternative embodiment, the polymerization occurs in two reaction zones, either in series or parallel.

Gas Phase Polymerization

Generally, in a fluidized gas bed process used for producing polymers, a gaseous stream containing one or more monomers (preferably C₃-C₄₀ olefin, ethylene, and diene) is continuously cycled through a fluidized bed in the presence

of a catalyst under reactive conditions. The gaseous stream is withdrawn from the fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and fresh monomer is added to replace the polymerized monomer. (See for example U.S. Pat. Nos. 4,543,399, 4,588,790, 5,028,670, 5,317,036, 5,352,749, 5,405,922, 5,436,304, 5,453,471, 5,462,999, 5,616,661 and 5,668,228 all of which are fully incorporated herein by reference.)

Slurry Phase Polymerization

A slurry polymerization process generally operates between 1 to about 50 atmosphere pressure range (15 psi to 735 psi, 103 kPa to 5068 kPa) or even greater and temperatures in the range of 0° C. to about 120° C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization diluent medium to which monomers (ethylene, a C₃-C₄₀ comonomer, and a diene) along with catalyst are added. The suspension including diluent is intermittently or continuously removed from the reactor where the volatile components are separated from the polymer and recycled, optionally after a distillation, to the reactor. The liquid diluent employed in the polymerization medium is typically an alkane having from 3 to 7 carbon atoms, preferably a branched alkane. The medium employed should be liquid under the conditions of polymerization and relatively inert. When a propane medium is used, the process must be operated above the reaction diluent critical temperature and pressure. Preferably, a hexane or an isobutane medium is employed.

In at least one embodiment, polymerization process is a particle form polymerization, or a slurry process, where the temperature is kept below the temperature at which the polymer goes into solution. Such technique is well known in the art, and described in for instance U.S. Pat. No. 3,248,179 which is fully incorporated herein by reference. The preferred temperature in the particle form process is within the range of about 85° C. to about 110° C. Two preferred polymerization methods for the slurry process are those using a loop reactor and those utilizing a plurality of stirred reactors in series, parallel, or combinations thereof. Non-limiting examples of slurry processes include continuous loop or stirred tank processes. Also, other examples of slurry processes are described in U.S. Pat. No. 4,613,484, which is herein fully incorporated by reference.

In another embodiment, the slurry process is carried out continuously in a loop reactor. The catalyst, as a slurry in isohexane or other diluent or as a dry free flowing powder, is injected regularly to the reactor loop, which is itself filled with circulating slurry of growing polymer particles in a diluent of isohexane or other diluent containing monomer and comonomer. Hydrogen, optionally, may be added as a molecular weight control. (In one embodiment hydrogen is added from 50 ppm to 500 ppm, such as from 100 ppm to 400 ppm, such as 150 ppm to 300 ppm.)

The reactor may be maintained at a pressure of up to 5000 kPa, such as 2,000 kPa to 5,000 kPa, such as from 3620 kPa to 4309 kPa, and at a temperature in the range of about 60° C. to about 120° C. depending on the desired polymer melting characteristics. Reaction heat is removed through the loop wall since much of the reactor is in the form of a double-jacketed pipe. The slurry is allowed to exit the reactor at regular intervals or continuously to a heated low pressure flash vessel, rotary dryer and a nitrogen purge column in sequence for removal of diluent (such as isohexane) and all unreacted monomer and comonomers. The resulting hydrocarbon free powder is then compounded for use in various applications.

Other additives may also be used in the polymerization, as desired, such as one or more scavengers, promoters, modifiers, chain transfer agents (such as diethyl zinc), reducing agents, oxidizing agents, hydrogen, aluminum alkyls, or silanes.

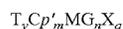
Useful chain transfer agents are typically alkylalumoxanes, a compound represented by the formula AlR_3 , ZnR_2 (where each R is, independently, a C₁-C₈ hydrocarbyl, preferably methyl, ethyl, propyl, butyl, pentyl, hexyl octyl or an isomer thereof). Examples can include diethyl zinc, methylalumoxane, trimethylaluminum, triisobutylaluminum, trioctylaluminum, or a combination thereof.

Solution Polymerization

In a preferred embodiment, the polymerization occurs in a solution polymerization process. A solution polymerization is a polymerization process in which the polymer is dissolved in a liquid polymerization medium, such as an inert solvent or monomer(s) or their blends. A solution polymerization is typically homogeneous. A homogeneous polymerization is one where the polymer product is dissolved in the polymerization medium. Such systems are preferably not turbid as described in J. Vladimir Oliveira, C. Dariva and J. C. Pinto, Ind. Eng. Chem. Res. 29, 2000, 4627. Generally solution polymerization involves polymerization in a continuous reactor in which the polymer formed and the starting monomer and catalyst materials supplied, are agitated to reduce or avoid concentration gradients and in which the monomer acts as a diluent or solvent or in which a hydrocarbon is used as a diluent or solvent. Suitable processes typically operate at temperatures from about 0° C. to about 250° C., preferably from about 10° C. to about 200° C., more preferably from about 40° C. to about 180° C., more preferably from about 50° C. to about 160° C., more preferably from about 60° C. to about 140° C. and at pressures of about 0.1 MPa or more, preferably 25 MPa or more. The upper pressure limit is not critically constrained but typically can be about 100 MPa or less, preferably, 50 MPa or less, preferably 25 MPa or less, preferably 20 MPa or less, preferably 15 MPa or less, preferably 12 MPa or less. Temperature control in the reactor can generally be obtained by balancing the heat of polymerization and with reactor cooling by reactor jackets or cooling coils to cool the contents of the reactor, auto refrigeration, pre-chilled feeds, vaporization of liquid medium (diluent, monomers or solvent) or combinations of all three. Adiabatic reactors with pre-chilled feeds can also be used. The purity, type, and amount of solvent can be optimized for the maximum catalyst productivity for a particular type of polymerization. The solvent can be also introduced as a catalyst carrier. The solvent can be introduced as a gas phase or as a liquid phase depending on the pressure and temperature. Advantageously, the solvent can be kept in the liquid phase and introduced as a liquid. Solvent can be introduced in the feed to the polymerization reactors.

Catalyst Compounds

The present disclosure provides polymerization processes where ethylene, C₃₊ olefin (such as C₃-C₄₀ α-olefin, preferably propylene), ethylene, and diene (such as ENB) are contacted with a catalyst system comprising an activator, optional support, and a catalyst compound. The catalyst compound, optional support and activator may be combined in any order, and are combined typically prior to contacting the catalyst system with the monomer. In at least one embodiment, the catalyst compound is represented by formula (I):



(I)

wherein:

Cp' is a tetrahydroindacenyl group (such as tetrahydro-s-indacenyl or tetrahydro-as-indacenyl) which is optionally substituted or unsubstituted, provided that when Cp' is tetrahydro-s-indacenyl: 1) the 3 and/or 4 positions are not aryl or substituted aryl, 2) the 3 position is not directly bonded to a group 15 or 16 heteroatom, 3) there are no additional rings fused to the tetrahydroindacenyl ligand, 4) T is not bonded to the 2-position, and 5) the 5, 6, or 7-position (preferably the 6 position) is geminally disubstituted, preferably with two C₁-C₁₀ alkyl groups; M is a group 2, 3, 4, 5, or 6 transition metal, preferably group 4 transition metal, for example titanium, zirconium, or hafnium (preferably titanium);

T is a bridging group (such as dialkylsilylene, dialkylcarbylene, phen-1,2-diyl, substituted phen-1,2-diyl, cyclohex-1,2-diyl or substituted cyclohex-1,2-diyl). T is preferably (CR⁸R⁹)X, SiR⁸R⁹ or GeR⁸R⁹ where x is 1 or 2, R⁸ and R⁹ are independently selected from hydrogen, substituted or unsubstituted hydrocarbyl, halocarbyl, silylcarbyl and germlylcarbyl and R⁸ and R⁹ may optionally be bonded together to form a ring structure, and in a particular embodiment, R⁸ and R⁹ are not aryl);

y is 0 or 1, indicating the absence or presence of T;

G is a heteroatom group represented by the formula JR_{z,y}ⁱ where J is N, P, O or S, R' is a C₁ to C₁₀₀ hydrocarbyl group (such as a C₁ to C₂₀ hydrocarbyl group), and z is 2 when J is N or P, and z is 1 when J is O or S (preferably J is N and z is 2) (R' can be a linear, branched or cyclic C₁ to C₂₀ hydrocarbyl group, preferably independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, phenyl, and isomers thereof, including t-butyl, cyclododecyl, cyclooctyl, preferably t-butyl and or cyclododecyl);

X is a leaving group (such as a halide, a hydride, an alkyl group, an alkenyl group or an arylalkyl group) and optionally two or more X may form a part of a fused ring or a ring system; m=1; n=1, 2 or 3; q=1, 2 or 3; and the sum of m+n+q is equal to the oxidation state of the transition metal (preferably 3, 4, 5, or 6, preferably 4); preferably m=1, n=1, q is 2, and y=1.

In at least one embodiment of formula (I), M is a group 4 transition metal (preferably Hf, Ti and/or Zr, preferably Ti). In at least one embodiment of formula (I), JR_{z,y}ⁱ is cyclododecyl amido, t-butyl amido, and or 1-adamantyl amido.

In at least one embodiment of formula (I), each X is, independently, selected from hydrocarbyl radicals having from 1 to 20 carbon atoms, aryls, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof, (two X's may form a part of a fused ring or a ring system), preferably each X is independently selected from halides, aryls and C₁ to C₅ alkyl groups, preferably each X is a benzyl, methyl, ethyl, propyl, butyl, pentyl, or chloro group.

In at least one embodiment of formula (I), the Cp' group may be substituted with a combination of subsequent groups R. R includes one or more of hydrogen, or linear, branched alkyl radicals, or alkenyl radicals, alkynyl radicals, cycloalkyl radicals or aryl radicals, acyl radicals, alkoxy radicals, aryloxy radicals, alkylthio radicals, dialkylamino radicals, alkoxycarbonyl radicals, aryloxy carbonyl radicals, carbamoyl radicals, alkyl- or dialkyl-carbamoyl radicals, acyloxy radicals, acylamino radicals, arylamino radicals, straight, branched or cyclic, alkylene radicals, or combination thereof. In at least one embodiment, substituent groups R have up to 50 non-hydrogen atoms, preferably from 1 to 30

carbon, that can also be substituted with halogens or heteroatoms or the like, provided that when Cp' is tetrahydro-s-indacenyl: 1) the 3 and/or 4 position is not aryl or substituted aryl, 2) the 3-position is not substituted with a group 15 or 16 heteroatom, 3) there are no additional rings fused to the tetrahydroindacenyl ligand, T is not bonded to the 2-position, and 5) the 5, 6, or 7-position (preferably the 6 position) is geminally disubstituted, preferably with two C₁-C₁₀ alkyl groups. Non-limiting examples of alkyl substituents R include methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopentyl, cyclohexyl, benzyl or phenyl groups and the like, including all their isomers, for example, tertiary butyl, isopropyl and the like. Other hydrocarbyl radicals include fluoromethyl, fluoroethyl, difluoroethyl, iodopropyl, bromohexyl chlorobenzyl and hydrocarbyl substituted organometalloid radicals including trimethylsilyl, trimethylgermyl, methyl-diethylsilyl and the like; and halocarbyl-substituted organometalloid radicals including tris (trifluoromethyl)silyl, methylbis(difluoromethyl)silyl, bromomethyl-dimethylgermyl and the like; and disubstituted boron radicals including dimethylboron for example; and disubstituted pnictogen radicals including dimethylamine, dimethylphosphine, diphenylamine, methylphenylphosphine, chalcogen radicals including methoxy, ethoxy, propoxy, phenoxy, methylsulfide and ethylsulfide. Non-hydrogen substituents R include the atoms carbon, silicon, boron, aluminum, nitrogen, phosphorus, oxygen, tin, sulfur, germanium and the like, including olefins such as, but not limited to, olefinically unsaturated substituents including vinyl-terminated ligands, for example but-3-enyl, prop-2-enyl, hex-5-enyl and the like.

In at least one embodiment of formula (I), the substituent(s) R are, independently, hydrocarbyl groups, heteroatoms, or heteroatom containing groups, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl or an isomer thereof, or a C₁ to C₂₀ hydrocarbyl substituted with an N, O, S and or P heteroatom or heteroatom containing group (typically having up to 12 atoms, including the N, O, S and P heteroatoms), provided that when Cp' is tetrahydro-s-indacenyl, the 3 and/or 4 position are not aryl or substituted aryl, the 3 position is not substituted with a group 15 or 16 heteroatom, and there are no additional rings fused to the tetrahydroindacenyl ligand, T is not bonded to the 2-position, and the 5, 6, or 7-position (preferably the 6 position) is geminally disubstituted, preferably with two C₁-C₁₀ alkyl groups.

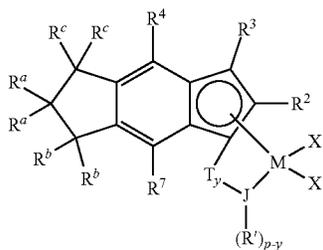
In at least one embodiment of formula (I), the Cp' group is tetrahydro-as-indacenyl or tetrahydro-s-indacenyl which may be substituted.

y can be 1 where T is a bridging group containing at least one group 13, 14, 15, or 16 element, in particular boron or a group 14, 15 or 16 element. Examples of suitable bridging groups include P(=S)R*, P(=Se)R*, P(=O)R*, R₂C, R₂Si, R₂Ge, R₂CCR₂*, R₂CCR₂CR₂*, R₂CCR₂CR₂CR₂*, R₂C=CR*, R₂C=CR*CR₂*, R₂CCR₂=CR*CR₂*, R₂C=CR*CR₂=CR*, R₂C=CR*CR₂CR₂*, R₂CSiR₂*, R₂CSiR₂SiR₂*, R₂SiOSiR₂*, R₂CSiR₂CR₂*, R₂SiCR₂SiR₂*, R₂C=CR*SiR₂*, R₂CGeR₂*, R₂GeGeR₂*, R₂CGeR₂CR₂*, R₂GeCR₂GeR₂*, R₂SiGeR₂*, R₂C=CR*GeR₂*, R₂B, R₂C—BR*, R₂C—BR*—CR₂*, R₂C—O—CR₂*, R₂CR₂C—O—CR₂CR₂*, R₂C—O—CR₂CR₂*, R₂C—O—CR*—CR₂*, R₂C—S—CR₂*, R₂CR₂C—S—CR₂CR₂*, R₂C—S—CR₂CR₂*, R₂C—S—CR*—CR₂*, R₂C—Se—CR₂*, R₂CR₂C—Se—CR₂CR₂*, R₂C—Se—CR₂CR₂*, R₂C—Se—CR*—CR₂*, R₂C—N=CR*, R₂C—NR*—

25

CR^*_2 , $R^*_2C-NR^*-CR^*_2CR^*_2$, $R^*_2C-NR^*-CR^*=CR^*$, $R^*_2CR^*_2C-NR^*-CR^*_2CR^*_2$, $R^*_2C-P=CR^*$, $R^*_2C-PR^*-CR^*_2$, O, S, Se, Te, NR^* , PR^* , AsR^* , SbR^* , O—O, S—S, R^*N-NR^* , R^*P-PR^* , O—S, O— NR^* , O— PR^* , S— NR^* , S— PR^* , and R^*N-PR^* where R^* is hydrogen or a C_1 - C_{20} containing hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germylcarbyl substituent, and optionally two or more adjacent R^* may join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, and optionally any one or more adjacent R^* and R' may join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent. Preferred examples for the bridging group T include — CH_2 —, — CH_2CH_2 —, — $SiMe_2$ —, — $SiPh_2$ —, — $Si(Me)(Ph)$ —, — $Si(CH_2)_3$ —, — $Si(CH_2)_4$ —, —O—, —S—, — $N(Ph)$ —, — $P(Ph)$ —, — $N(Me)$ —, — $P(Me)$ —, — $N(Et)$ —, — $N(Pr)$ —, — $N(Bu)$ —, — $P(Et)$ —, — $P(Pr)$ —, — $(Me)_2SiOSi(Me)_2$ —, and — $P(Bu)$ —. In a preferred embodiment of the present disclosure, when Cp' is tetrahydro-s-indaceny and T is R^*_2Si , then R^* is not aryl. In some embodiments, R^* is not aryl or substituted aryl.

In at least one embodiment, the catalyst compound is one or more bridged transition metal compounds represented by formula (II):



where M is a group 4 metal (such as Hf, Ti or Zr, preferably Ti);

J is N, O, S or P;

p is 2 when J is N or P, and is 1 when J is O or S (preferably J is N, y=1, and p=2);

each R^a is independently C_1 - C_{10} alkyl (alternately a C_2 - C_{10} alkyl);

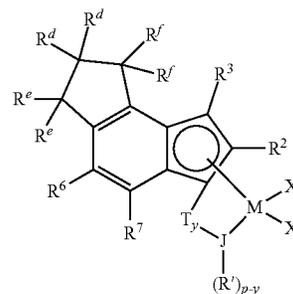
each R^b and each R^c is independently hydrogen or a C_1 - C_{10} alkyl (alternately a C_2 - C_{10} alkyl);

each R^2 , R^3 , R^4 , and R^7 is independently hydrogen, or a C_1 - C_{50} substituted or unsubstituted hydrocarbyl, halocarbyl, silylcarbyl or germylcarbyl, provided that: 1) R^3 and/or R^4 are not aryl or substituted aryl, 2) R^3 is not directly bonded to a group 15 or 16 heteroatom, and 3) adjacent R^4 , R^c , R^a , R^b , or R^7 do not join together to form a fused ring system; each R' is, independently, a C_1 - C_{100} substituted or unsubstituted hydrocarbyl, halocarbyl, silylcarbyl or germylcarbyl;

T is a bridging group and y is 0 or 1 indicating the absence (y=0) or presence (y=1) of T; and each X is, independently, a leaving group, or two Xs are joined and bound to the metal atom to form a metallocycle ring, or two Xs are joined to form a chelating ligand, a diene ligand, or an alkylidene.

In at least one embodiment, the catalyst compound is one or more bridged transition metal compounds represented by formula (III):

26



(III)

where M is a group 4 metal (such as Hf, Ti or Zr, preferably Ti);

J is N, O, S or P;

p is 2 when J is N or P, and is 1 when J is O or S (preferably J is N, y=1, and p=2);

each R^d , R^e and R^f are independently hydrogen or a C_1 - C_{10} alkyl (alternately a C_2 - C_{10} alkyl);

each R^2 , R^3 , R^6 , and R^7 is independently hydrogen, or a C_1 - C_{50} substituted or unsubstituted hydrocarbyl, halocarbyl, silylcarbyl or germylcarbyl;

each R' is, independently, a C_1 - C_{100} substituted or unsubstituted hydrocarbyl, halocarbyl, silylcarbyl or germylcarbyl;

T is a bridging group and y is 0 or 1 indicating the absence (y=0) or presence (y=1) of T;

and each X is, independently, a leaving group, or two Xs are joined and bound to the metal atom to form a metallocycle ring, or two Xs are joined to form a chelating ligand, a diene ligand, or an alkylidene.

In some embodiments of formulae II and III, y is 1 and T is $(CR^8R^9)_x$, SiR^8R^9 or GeR^8R^9 where x is 1 or 2, R^8 and R^9 are independently selected from hydrogen or substituted or unsubstituted hydrocarbyl, halocarbyl, silylcarbyl and germylcarbyl and R^8 and R^9 may optionally be bonded together to form a ring structure.

In at least one embodiment of the present disclosure, each R^2 , R^3 , R^6 , and R^7 is independently hydrogen, or a C_1 - C_{50} substituted or unsubstituted hydrocarbyl, halocarbyl, silylcarbyl or germylcarbyl, preferably methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, and dodecyl or an isomer thereof.

In at least one embodiment of the present disclosure, each R^2 , R^3 , R^4 , and R^7 is independently hydrogen, or a C_1 - C_{50} substituted or unsubstituted hydrocarbyl, halocarbyl, silylcarbyl or germylcarbyl, preferably methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, and dodecyl or an isomer thereof.

In at least one embodiment of the present disclosure, each R^a or R^d is independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof, preferably methyl and ethyl, preferably methyl.

In at least one embodiment of the present disclosure, each R^b , R^c , R^e or R^f is independently selected from hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof, preferably hydrogen or methyl, preferably hydrogen.

In at least one embodiment of the present disclosure, each R^a is independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof, preferably methyl and ethyl, preferably methyl, and each R^b and R^c are independently selected from hydrogen,

methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof, preferably hydrogen or methyl, preferably hydrogen.

In at least one embodiment of the present disclosure, each R^d is independently selected from hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof, preferably methyl and ethyl, preferably methyl, and each R^e and R^f are independently selected from hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof, preferably hydrogen or methyl, preferably hydrogen.

In at least one embodiment of the present disclosure, each R^a , R^b and R^c are independently selected from hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof, preferably hydrogen or methyl.

In at least one embodiment of the present disclosure, each R^d , R^e and R^f are independently selected from hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof, preferably hydrogen or methyl.

In at least one embodiment of the present disclosure, R is a C_1 - C_{100} substituted or unsubstituted hydrocarbyl, halocarbyl, or silylcarbyl, preferably methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, phenyl or an isomer thereof, preferably t-butyl, neopentyl, cyclohexyl, cyclooctyl, cyclododecyl, adamantyl, or norbornyl.

In at least one embodiment of the present disclosure, T is CR^8R^9 , R^8R^9C — CR^8R^9 , SiR^8R^9 or GeR^8R^9 where R^8 and R^9 are independently selected from hydrogen or substituted or unsubstituted hydrocarbyl, halocarbyl, silylcarbyl and R^8 and R^9 may optionally be bonded together to form a ring structure, preferably each R^8 and R^9 is independently methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, benzyl, phenyl, methylphenyl or an isomer thereof, preferably methyl, ethyl, propyl, butyl, or hexyl. When R^8 and R^9 are optionally bonded together preferred bridges include substituted or unsubstituted phen-1,2-diyl, cyclohex-1,2-diyl, cyclopentamethylenesilylene, cyclotetramethylenesilylene, cyclotrimethylenesilylene and dibenzo[b,d]silolyl. Additionally, optionally any one or more adjacent R^8 and/or R^9 may join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent along with R^1 .

In at least one embodiment of the present disclosure, at least one of R^8 or R^9 is not aryl. In at least one embodiment of the present disclosure, R^8 is not aryl. In at least one embodiment of the present disclosure, R^9 is not aryl. In at least one embodiment of the present disclosure, R^8 and R^9 are not aryl.

In at least one embodiment of the present disclosure, R^8 and R^9 are independently C_1 - C_{10} alkyl, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, or an isomer thereof.

In at least one embodiment of the present disclosure, each R^2 , R^3 , R^4 , and R^7 is independently hydrogen or hydrocarbyl. Each R^2 , R^3 , R^4 , and R^7 can be independently hydrogen or a C_1 - C_{10} alkyl, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, or an isomer thereof.

In at least one embodiment of the present disclosure, each R^2 , R^3 , R^6 , and R^7 is independently hydrogen or hydrocarbyl. Each R^2 , R^3 , R^6 , and R^7 can be independently hydrogen or a C_1 - C_{10} alkyl, preferably methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, or an isomer thereof.

In at least one embodiment of the present disclosure, R^2 is a C_1 - C_{10} alkyl and R^3 , R^4 , and R^7 are hydrogen.

In at least one embodiment of the present disclosure, R^2 is a C_1 - C_{10} alkyl and R^3 , R^6 , and R^7 are hydrogen.

In at least one embodiment of the present disclosure, R^2 , R^3 , R^4 , and R^7 are hydrogen. In at least one embodiment of the present disclosure, R^2 , R^3 , R^6 , and R^7 are hydrogen.

In at least one embodiment of the present disclosure, R^2 is methyl, ethyl, or an isomer of propyl, butyl, pentyl or hexyl, and R^3 , R^4 , and R^7 are hydrogen. In at least one embodiment of the present disclosure, R^2 is methyl, ethyl, or an isomer of propyl, butyl, pentyl or hexyl, and R^3 , R^6 , and R^7 are hydrogen.

In at least one embodiment of the present disclosure, R^2 is methyl and R^3 , R^4 , and R^7 are hydrogen. In at least one embodiment of the present disclosure, R^2 is methyl and R^3 , R^6 , and R^7 are hydrogen.

In at least one embodiment of the present disclosure, R^3 is hydrogen. In at least one embodiment of the present disclosure, R^2 is hydrogen.

In at least one embodiment of the present disclosure, R^2 and each R^a is independently a C_1 - C_{10} alkyl and R^3 , R^4 , R^7 and each R^b and R^c are hydrogen.

In at least one embodiment of the present disclosure, R^2 and each R^d is a C_1 - C_{10} alkyl and R^3 , R^6 , R^7 and each R^e and R^f are hydrogen.

In at least one embodiment of the present disclosure, R^2 and each R^a is independently a methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, or an isomer thereof, and R^3 , R^4 , R^7 and each R^b and R^c are hydrogen.

In at least one embodiment of the present disclosure, R^2 and each R^d is a methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, or an isomer thereof, and R^3 , R^6 , R^7 and each R^e and R^f are hydrogen.

In at least one embodiment of the present disclosure, R^1 is C_1 - C_{100} or C_1 - C_{30} substituted or unsubstituted hydrocarbyl.

In at least one embodiment of the present disclosure, R is C_1 - C_{30} substituted or unsubstituted alkyl (linear, branched, or cyclic), aryl, alkaryl, or heterocyclic group. In at least one embodiment of the present disclosure, R^1 is C_1 - C_{30} linear, branched or cyclic alkyl group.

In at least one embodiment of the present disclosure, R is methyl, ethyl, or any isomer of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl. In at least one embodiment of the present disclosure, R^1 is a cyclic or polycyclic hydrocarbyl.

In at least one embodiment of the present disclosure, R^1 is selected from tert-butyl, neopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl, cyclododecyl, adamantyl, and norbornyl. In at least one embodiment, R^1 is tert-butyl.

In at least one embodiment of the present disclosure, R^1 is selected from tert-butyl, neopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl, cyclododecyl, adamantyl, and norbornyl. In at least one embodiment, R^1 is tert-butyl.

In at least one embodiment of the present disclosure, T is selected from diphenylmethylenes, dimethylmethylenes, 1,2-ethylene, phen-1,2-diyl, cyclohex-1,2-diyl, cyclotrimethylenesilylene, cyclotetramethylenesilylene, cyclopentamethylenesilylene, dibenzo[b,d]silolyl, dimethylsilylene, diethylsilylene, methylethylsilylene, and dipropylsilylene.

In at least one embodiment of the present disclosure, each R^a is independently methyl, ethyl, propyl, butyl, pentyl or hexyl. In at least one embodiment of the present disclosure, each R^a is independently methyl or ethyl. Each R^a can be methyl.

In at least one embodiment of the present disclosure, each R^d is independently methyl, ethyl, propyl, butyl, pentyl or hexyl. In at least one embodiment of the present disclosure, each R^d is independently methyl or ethyl. Each R^d can be methyl.

In at least one embodiment of the present disclosure, each R^d and each R^e and R^f are independently hydrogen, methyl, ethyl, propyl, butyl, pentyl or hexyl. In at least one embodiment of the present disclosure, each R^d is independently hydrogen, methyl, or ethyl.

In at least one embodiment of the present disclosure, each R^b and R^c is hydrogen.

In at least one embodiment of the present disclosure, each R^e and R^f is hydrogen.

In at least one embodiment of the present disclosure, each X is hydrocarbyl, halocarbyl, or substituted hydrocarbyl or halocarbyl.

In at least one embodiment of the present disclosure, X is methyl, benzyl, or halo where halo includes fluoro, chloro, bromo and iodido.

In at least one embodiment of the present disclosure, both X are joined together to form a C_4 - C_{20} diene ligand such as 1,3-butadiene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, 2,4-dimethylpentadiene and the like.

In at least one embodiment of formula (II) of the present disclosure: 1) R^3 and/or R^4 are not aryl or substituted aryl, 2) R^3 is not directly bonded to a group 15 or 16 heteroatom, and 3) adjacent R^4 , R^c , R^a , R^b , or R^7 do not join together to form a fused ring system, and 4) each R^a is a C_1 to C_{10} alkyl (preferably methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, or an isomer thereof).

In a preferred embodiment of the present disclosure, T of any of formulas (I)-(III) is represented by the formula ER^g_2 or $(ER^g_2)_2$, where E is C, Si, or Ge, and each R^g is, independently, hydrogen, halogen, C_1 to C_{20} hydrocarbyl (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl) or a C_1 to C_{20} substituted hydrocarbyl, and two R^g can form a cyclic structure including aromatic, partially saturated, or saturated cyclic or fused ring system. Preferably, T is a bridging group comprising carbon or silica, such as dialkylsilyl, preferably T is selected from $-CH_2-$, $-CH_2CH_2-$, $-C(CH_3)_2-$, $Si(Me)_2$, cyclotrimethylenesilylene ($-Si(CH_2)_3-$), cyclopentamethylenesilylene ($-Si(CH_2)_5-$) and cyclotetramethylenesilylene ($-Si(CH_2)_4-$).

In at least one embodiment, a catalyst compound is one or more of: dimethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(t-butylamido)M(R)₂; dimethylsilylene(6,6-dimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(t-butylamido)M(R)₂; dimethylsilylene(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)M(R)₂; dimethylsilylene(7,7-dimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)M(R)₂; dimethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(6,6-dimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(7,7-dimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(cyclohexylamido)M(R)₂; dimethylsilylene(6,6-dimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(cyclohexylamido)M(R)₂; dimethylsilylene(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclohexylamido)M(R)₂; dimethylsilylene(7,7-dimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclohexylamido)M(R)₂; dimethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-in-

dacen-1-yl)(adamantylamido)M(R)₂; dimethylsilylene(6,6-dimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(adamantylamido)M(R)₂; dimethylsilylene(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(adamantylamido)M(R)₂; dimethylsilylene(7,7-dimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(adamantylamido)M(R)₂; dimethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(neopentylamido)M(R)₂; dimethylsilylene(6,6-dimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(neopentylamido)M(R)₂; dimethylsilylene(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(neopentylamido)M(R)₂; dimethylsilylene(7,7-dimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(neopentylamido)M(R)₂; dimethylsilylene(2-methyl-6,6-diethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(t-butylamido)M(R)₂; dimethylsilylene(6,6-diethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(t-butylamido)M(R)₂; dimethylsilylene(2-methyl-7,7-diethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)M(R)₂; dimethylsilylene(7,7-diethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)M(R)₂; dimethylsilylene(2-methyl-6,6-diethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(6,6-diethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(2-methyl-7,7-diethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(7,7-dimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclododecylamido)M(R)₂; diethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(t-butylamido)M(R)₂; diethylsilylene(6,6-dimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(t-butylamido)M(R)₂; diethylsilylene(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)M(R)₂; diethylsilylene(7,7-dimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)M(R)₂; dimethylsilylene(2-methyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclohexylamido)M(R)₂; dimethylsilylene(2-methyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(2-methyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(adamantylamido)M(R)₂; and dimethylsilylene(2-methyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)M(R)₂, where M is selected from Ti, Zr, and Hf and R is selected from halogen or C_1 to C_5 alkyl, preferably R is a methyl group or a halogen group, preferably M is Ti.

In alternative embodiments, a catalyst system can include two or more different transition metal compounds. For purposes of the present disclosure one transition metal compound is considered different from another if they differ by at least one atom. For example “ $Me_2Si(2,7,7-Me_3-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclohexylamido)TiCl_2$ ” is different from $Me_2Si(2,7,7-Me_3-3,6,7,8-tetrahydro-as-indacen-3-yl)(n-butylamido)TiCl_2$ ” which is different from $Me_2Si(2,7,7-Me_3-3,6,7,8-tetrahydro-as-indacen-3-yl)(n-butylamido)HfCl_2$.

In some embodiments, formulae I through III are referred to as mono-tetrahydroindacenyl compounds, precatalysts and/or catalysts.

In at least one embodiment, one mono-tetrahydroindacenyl compound as described herein is used in the catalyst system.

Activators

The terms “cocatalyst” and “activator” are used herein interchangeably and include a compound which can activate any one of the catalyst compounds described above by converting the neutral catalyst compound to a catalytically active catalyst compound cation. Non-limiting activators, for example, include alumoxanes, aluminum alkyls, ionizing activators, which may be neutral or ionic, and conventional-type cocatalysts. Preferred activators typically include non-

coordinating anion compounds, alumoxane compounds, modified alumoxane compounds, and ionizing anion precursor compounds that abstract a reactive, 6-bound, metal ligand making the metal complex cationic and providing a charge-balancing noncoordinating or weakly coordinating anion.

Alumoxane Activators

Alumoxane activators are utilized as activators in the catalyst systems described herein. Alumoxanes are generally oligomeric compounds containing $-\text{Al}(\text{R}^1)-\text{O}-$ subunits, where R^1 is an alkyl group. Examples of alumoxanes include methylalumoxane (MAO), modified methylalumoxane (MMAO), ethylalumoxane and isobutylalumoxane. Alkylalumoxanes and modified alkylalumoxanes are suitable as catalyst activators, particularly when the abstractable ligand is an alkyl, halide, alkoxide or amide. Mixtures of different alumoxanes and modified alumoxanes may also be used. It may be preferable to use a visually clear methylalumoxane. A cloudy or gelled alumoxane can be filtered to produce a clear solution or clear alumoxane can be decanted from the cloudy solution. A useful alumoxane is a modified methyl alumoxane (MMAO) cocatalyst type 3A (commercially available from Akzo Chemicals, Inc. under the trade name Modified Methylalumoxane type 3A, covered under patent number U.S. Pat. No. 5,041,584).

When the activator is an alumoxane (modified or unmodified), some embodiments select the maximum amount of activator typically at up to a 5000-fold molar excess Al/M over the catalyst compound (per metal catalytic site). The minimum activator-to-catalyst-compound is a 1:1 molar ratio. Alternate preferred ranges include from 1:1 to 500:1, alternately from 1:1 to 200:1, alternately from 1:1 to 100:1, or alternately from 1:1 to 50:1.

Non Coordinating Anion Activators

Non-coordinating anion activators may also be used herein. The term "non-coordinating anion" (NCA) means an anion which either does not coordinate to a cation or which is only weakly coordinated to a cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base. "Compatible" non-coordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral transition metal compound and a neutral byproduct from the anion. Non-coordinating anions useful in accordance with the present disclosure are those that are compatible, stabilize the transition metal cation in the sense of balancing its ionic charge at +1, and yet retain sufficient lability to permit displacement during polymerization.

It is within the scope of the present disclosure to use an ionizing activator, neutral or ionic, such as tri (n-butyl) ammonium tetrakis (pentafluorophenyl) borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, a tris perfluorophenyl boron metalloid precursor or a tris perfluoronaphthyl boron metalloid precursor, polyhalogenated heteroborane anions (WO 98/43983), boric acid (U.S. Pat. No. 5,942,459), alone or in combination with the alumoxane or modified alumoxane activators. It is also within the scope of the present disclosure to use neutral or ionic activators in combination with the alumoxane or modified alumoxane activators.

The catalyst systems of the present disclosure can include at least one non-coordinating anion (NCA) activator. Specifically the catalyst systems may include NCAs which either do not coordinate to a cation or which only weakly

coordinate to a cation thereby remaining sufficiently labile to be displaced during polymerization.

In a preferred embodiment boron containing NCA activators represented by the formula below can be used:



where: Z is (L-H) or a reducible Lewis acid; L is a neutral Lewis base; H is hydrogen; (L-H) is a Bronsted acid; A^{d-} is a boron containing non-coordinating anion having the charge d-; d is 1, 2, or 3.

The cation component, Z_d^+ may include Bronsted acids such as protons or protonated Lewis bases or reducible Lewis acids capable of protonating or abstracting a moiety, such as an alkyl or aryl, from the bulky ligand metallocene containing transition metal catalyst precursor, resulting in a cationic transition metal species.

The activating cation Z_d^+ may also be a moiety such as silver, tropylium, carboniums, ferroceniums and mixtures, preferably carboniums and ferroceniums. Most preferably Z_d^+ is triphenyl carbonium. Preferred reducible Lewis acids can be any triaryl carbonium (where the aryl can be substituted or unsubstituted, such as those represented by the formula: (Ar_3C^+) , where Ar is aryl or aryl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C_1 to C_{40} hydrocarbyl), preferably the reducible Lewis acids as "Z" include those represented by the formula: (Ph_3C) , where Ph is a substituted or unsubstituted phenyl, preferably substituted with C_1 to C_{40} hydrocarbyls or substituted a C_1 to C_{40} hydrocarbyls, preferably C_1 to C_{20} alkyls or aromatics or substituted C_1 to C_{20} alkyls or aromatics, preferably Z is a triphenylcarbonium.

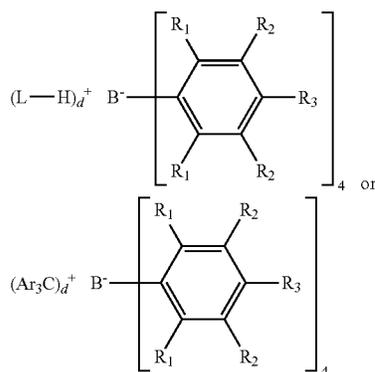
When Z_d^+ is the activating cation $(\text{L-H})_d^+$, it is preferably a Bronsted acid, capable of donating a proton to the transition metal catalytic precursor resulting in a transition metal cation, including ammoniums, oxoniums, phosphoniums, silyliums, and mixtures thereof, preferably ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyridine, p-bromo N,N-dimethylaniline, p-nitro-N,N-dimethylaniline, phosphoniums from triethylphosphine, triphenylphosphine, and diphenylphosphine, oxoniums from ethers such as dimethyl ether diethyl ether, tetrahydrofuran and dioxane, sulfoniums from thioethers, such as diethyl thioethers, tetrahydrothiophene, and mixtures thereof.

The anion component A^{d-} includes those having the formula $[\text{M}^{k+}\text{Q}_n]^{d-}$ wherein k is 1, 2, or 3; n is 1, 2, 3, 4, 5, or 6 (preferably 1, 2, 3, or 4); $n-k=d$; M is an element selected from group 13 of the Periodic Table of the Elements, preferably boron or aluminum, and Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstituted-hydrocarbyl radicals, said Q having up to 20 carbon atoms with the proviso that in not more than 1 occurrence is Q a halide. Preferably, each Q is a fluorinated hydrocarbyl group having 1 to 20 carbon atoms, more preferably each Q is a fluorinated aryl group, and most preferably each Q is a pentafluoryl aryl group. Examples of suitable A^{d-} also include diboron compounds as disclosed in U.S. Pat. No. 5,447,895, which is fully incorporated herein by reference.

Illustrative, but not limiting examples of boron compounds which may be used as an activating cocatalyst are the compounds described as (and particularly those specifically listed as) activators in U.S. Pat. No. 8,658,556, which is incorporated by reference herein.

Most preferably, the ionic activator Z_d^+ (A^{d-}) is one or more of N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl) borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl) borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, or triphenylcarbenium tetra(perfluorophenyl)borate.

Bulky activators are also useful herein as NCAs. "Bulky activator" as used herein refers to anionic activators represented by the formula:



where: each R_1 is, independently, a halide, preferably a fluoride; Ar is substituted or unsubstituted aryl group (preferably a substituted or unsubstituted phenyl), preferably substituted with C_1 to C_{40} hydrocarbyls, preferably C_1 to C_{20} alkyls or aromatics; each R_2 is, independently, a halide, a C_6 to C_{20} substituted aromatic hydrocarbyl group or a siloxy group of the formula $-O-Si-R_a$, where R_a is a C_1 to C_{20} hydrocarbyl or hydrocarbylsilyl group (preferably R_2 is a fluoride or a perfluorinated phenyl group); each R_3 is a halide, C_6 to C_{20} substituted aromatic hydrocarbyl group or a siloxy group of the formula $-O-Si-R_a$, where R_a is a C_1 to C_{20} hydrocarbyl or hydrocarbylsilyl group (preferably R_3 is a fluoride or a C_6 perfluorinated aromatic hydrocarbyl group); wherein R_2 and R_3 can form one or more saturated or unsaturated, substituted or unsubstituted rings (preferably R_2 and R_3 form a perfluorinated phenyl ring); and L is an neutral Lewis base; $(L-H)^+$ is a Bronsted acid; d is 1, 2, or 3; wherein the anion has a molecular weight of greater than 1020 g/mol; wherein at least three of the substituents on the B atom each have a molecular volume of greater than 250 cubic A, alternately greater than 300 cubic A, or alternately greater than 500 cubic A.

Preferably $(Ar_3C)_d^+$ is $(Ph_3C)_d^+$, where Ph is a substituted or unsubstituted phenyl, preferably substituted with C_1 to C_{40} hydrocarbyls or substituted C_1 to C_{40} hydrocarbyls, preferably C_1 to C_{20} alkyls or aromatics or substituted C_1 to C_{20} alkyls or aromatics.

"Molecular volume" is used herein as an approximation of spatial steric bulk of an activator molecule in solution. Comparison of substituents with differing molecular volumes allows the substituent with the smaller molecular volume to be considered "less bulky" in comparison to the substituent with the larger molecular volume. Conversely, a substituent with a larger molecular volume may be considered "more bulky" than a substituent with a smaller molecular volume.

Molecular volume may be calculated as reported in "A Simple "Back of the Envelope" Method for Estimating the Densities and Molecular Volumes of Liquids and Solids," Journal of Chemical Education, Vol. 71, No. 11, November 1994, pp. 962-964. Molecular volume (MV), in units of cubic A, is calculated using the formula: $MV=8.3V_s$, where V_s is the scaled volume. V_s is the sum of the relative volumes of the constituent atoms, and is calculated from the molecular formula of the substituent using the following table of relative volumes. For fused rings, the V_s is decreased by 7.5% per fused ring.

Element	Relative Volume
H	1
1 st short period, Li to F	2
2 nd short period, Na to Cl	4
1 st long period, K to Br	5
2 nd long period, Rb to I	7.5
3 rd long period, Cs to Bi	9

For a list of particularly useful Bulky activators please see U.S. Pat. No. 8,658,556, which is incorporated by reference herein.

In another embodiment, one or more of the NCA activators is chosen from the activators described in U.S. Pat. No. 6,211,105.

Preferred activators include N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorophenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluorophenyl)borate, $Me_3NH^+[B(C_6F_5)_4^-]$; 1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl)pyrrolidinium; and tetrakis(pentafluorophenyl)borate, and 4-(tris (pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridine.

In at least one embodiment, the activator comprises a triaryl carbonium (such as triphenylcarbenium tetraphenylborate, triphenylcarbenium tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis(2,3,4,6-tetrafluorophenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(perfluorophenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

In another embodiment, the activator comprises one or more of trialkylammonium tetrakis(pentafluorophenyl)borate, N,N-dialkylanilinium tetrakis(pentafluorophenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl)borate, trialkylammonium tetrakis-(2,3,4,6-tetrafluorophenyl) borate, N,N-dialkylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, trialkylammonium tetrakis(perfluoronaphthyl)borate, N,N-dialkylanilinium tetrakis(perfluoronaphthyl)borate, trialkylammonium tetrakis(perfluorobiphenyl)borate, N,N-dialkylanilinium tetrakis(perfluorobiphenyl)borate, trialkylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dialkylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dialkylanilinium tetrakis(2,4,6-trimethylanilinium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate, (where alkyl is methyl, ethyl, propyl, n-butyl, sec-butyl, or t-butyl).

In preferred embodiments of the invention, N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate is the preferred activator.

The typical NCA activator-to-catalyst ratio, e.g., all NCA activators-to-catalyst ratio is about a 1:1 molar ratio. Alternate preferred ranges include from 0.1:1 to 100:1, alternately from 0.5:1 to 200:1, alternately from 1:1 to 500:1 alternately from 1:1 to 1000:1. A particularly useful range is from 0.5:1 to 10:1, preferably 1:1 to 5:1.

Activators useful herein also include those described in U.S. Pat. No. 7,247,687 at column 169, line 50 to column 174, line 43, particularly column 172, line 24 to column 173, line 53.

It is also within the scope of the present disclosure that the catalyst compounds can be combined with combinations of alumoxanes and NCA's (see for example, U.S. Pat. Nos. 5,153,157; 5,453,410; EP 0 573 120 B1; WO 94/07928; and WO 95/14044 which discuss the use of an alumoxane in combination with an ionizing activator).

Optional Scavengers or Co-Activators

In addition to the activator compounds, scavengers, chain transfer agents or co-activators may be used. Aluminum alkyl or organoaluminum compounds which may be utilized as scavengers or co-activators include, for example, trimethylaluminum, triethylaluminum, triisobutylaluminum, trin-hexylaluminum, tri-n-octylaluminum, and diethyl zinc.

Useful chain transfer agents that may also be used herein are typically a compound represented by the formula AlR_3 , ZnR_2 (where each R is, independently, a C_1 - C_8 aliphatic radical, preferably methyl, ethyl, propyl, butyl, pentyl, hexyl octyl or an isomer thereof) or a combination thereof, such as diethyl zinc, trimethylaluminum, triisobutylaluminum, tri-octylaluminum, or a combination thereof.

Supports

In some embodiments, the catalyst compounds described herein may be supported (with or without an activator) by any method effective to support other coordination catalyst systems, effective meaning that the catalyst so prepared can be used for oligomerizing or polymerizing olefin in a heterogeneous process. The catalyst precursor, activator, co-activator if needed, suitable solvent, and support may be added in any order or simultaneously. Typically, the complex and activator may be combined in solvent to form a solution. Then the support is added, and the mixture is stirred for 1 minute to 10 hours. The total solution volume may be greater than the pore volume of the support, but some embodiments limit the total solution volume below that needed to form a gel or slurry (about 90% to 400%, preferably about 100-200% of the pore volume). After stirring, the residual solvent is removed under vacuum, typically at ambient temperature and over 10-16 hours. But greater or lesser times and temperatures are possible.

The complex may also be supported absent the activator; in that case, the activator (and co-activator if needed) is added to a polymerization process's liquid phase. Additionally, two or more different complexes may be supported on the same support. Likewise, two or more activators or an activator and co-activator may be supported on the same support.

Suitable solid particle supports are typically comprised of polymeric or refractory oxide materials, each being preferably porous. A support material can have an average particle size greater than 10 μm for use in embodiments of the present disclosure. VA support material can be a porous support material, such as, talc, inorganic oxides, inorganic chlorides, for example magnesium chloride and resinous support materials such as polystyrene polyolefin or poly-

meric compounds or any other organic support material and the like. A support material can be an inorganic oxide material including group-2, -3, -4, -5, -13, or -14 metal or metalloid oxides. A catalyst support materials can be silica, alumina, silica-alumina, and their mixtures. Other inorganic oxides may serve either alone or in combination with the silica, alumina, or silica-alumina. These are magnesia, titania, zirconia, and the like. Lewis acidic materials such as montmorillonite and similar clays may also serve as a support. In this case, the support can optionally double as the activator component, however, an additional activator may also be used.

The support material may be pretreated by any number of methods. For example, inorganic oxides may be calcined, chemically treated with dehydroxylating agents such as aluminum alkyls and the like, or both.

As stated above, polymeric carriers will also be suitable in accordance with the present disclosure, see for example the descriptions in WO 95/15815 and U.S. Pat. No. 5,427, 991. The methods disclosed may be used with the catalyst complexes, activators or catalyst systems of the present disclosure to adsorb or absorb them on the polymeric supports, particularly if made up of porous particles, or may be chemically bound through functional groups bound to or in the polymer chains.

Useful supports typically have a surface area of from 10-700 m^2/g , a pore volume of 0.1-4.0 cc/g and an average particle size of 10-500 μm . Some embodiments select a surface area of 50-500 m^2/g , a pore volume of 0.5-3.5 cc/g, or an average particle size of 20-200 μm . Other embodiments select a surface area of 100-400 m^2/g , a pore volume of 0.8-3.0 cc/g, and an average particle size of 30-100 μm . Useful supports typically have a pore size of 10-1000 Angstroms, alternatively 50-500 Angstroms, or 75-350 Angstroms.

The catalyst complexes described herein are generally deposited on the support at a loading level of 10-100 micromoles of complex per gram of solid support; alternately 20-80 micromoles of complex per gram of solid support; or 40-60 micromoles of complex per gram of support. But greater or lesser values may be used provided that the total amount of solid complex does not exceed the support's pore volume.

In an alternative embodiment, catalyst complexes and catalyst systems described herein may be present on a fluorided support, e.g. a support, desirably particulate and porous, which has been treated with at least one inorganic fluorine containing compound. For example, the fluorided support composition can be a silicon dioxide support wherein a portion of the silica hydroxyl groups has been replaced with fluorine or fluorine containing compounds. For example, a useful support herein, is a silica support treated with ammonium hexafluorosilicate and/or ammonium tetrafluoroborate fluorine compounds. Typically the fluorine concentration present on the support is in the range of from 0.1 to 25 wt %, alternately 0.19 to 19 wt %, alternately from 0.6 to 3.5 wt %, based upon the weight of the support.

In an embodiment of the present disclosure, the catalyst system comprises fluorided silica, alkylalumoxane activator, and the bridged monocyclopentadienyl group 4 transition metal compound, where the fluorided support has not been calcined at a temperature of 400° C. or more.

The catalyst compound may be present on a support at 1 to 100 $\mu mol/g$ supported catalyst, preferably 20-60 $\mu mol/g$ supported catalyst.

37

The present disclosure also relates to metallocene catalyst systems comprising the reaction product of at least three components: (1) one or more bridged metallocenes having one tetrahydroindacenyl group; (2) one or more alkylaluminum or NCA activator; and (3) one or more fluorided support compositions, where the fluorided support composition has not been calcined at 400° C. or more, preferably the fluorided support composition has been calcined at a temperature of 100° C. to 395° C., alternately 125° C. to 350° C., alternately 150° C. to 300° C.).

Typically, the fluorided supports described herein are prepared by combining a solution of polar solvent (such as water) and fluorinating agent (such as SiF₄ or (NH₄)₂SiF₆) with a slurry of support (such as a toluene slurry of silica), then drying until it is free flowing, and optionally, calcining (typically at temperatures over 100° C. for at least 1 hour). The supports are then combined with activator(s) and catalyst compound (separately or together).

For more information on fluorided supports and methods to prepare them, please see U.S. Ser. No. 62/149,799, filed Apr. 20, 2015 (and all cases claiming priority to or the benefit of U.S. Ser. No. 62/149,799); U.S. Ser. No. 62/103,372, filed Jan. 14, 2015 (and all cases claiming priority to or the benefit of U.S. Ser. No. 62/103,372); and PCT/US2015/067582, filed Dec. 28, 2015 which are incorporated by reference herein.

This invention also relates to:

1. A method for producing an olefin polymer comprising:

contacting C₃-C₄₀ olefin, ethylene, and diene with a catalyst system comprising activator and a catalyst compound represented by formula (I):



wherein:

Cp' is a tetrahydroindacenyl group (preferably tetrahydro-s-indacenyl or tetrahydro-as-indacenyl) which is optionally substituted or unsubstituted, provided that when Cp' is tetrahydro-s-indacenyl: 1) the 3 and/or 4 positions are not aryl or substituted aryl, 2) the 3 position is not directly bonded to a group 15 or 16 heteroatom, 3) there are no additional rings fused to the tetrahydroindacenyl ligand, 4) T is not bonded to the 2-position, and 5) the 5, 6, or 7-position is geminally disubstituted;

M is a group 3, 4, 5, or 6 transition metal;

T is a bridging group;

y is 0 or 1, indicating the absence or presence of T;

G is a heteroatom group represented by the formula JR_{z-y}ⁱ where J is N, P, O or S,

Rⁱ is a C₁ to C₁₀₀ hydrocarbyl group, and z is 2 when J is N or P, and z is 1 when J is O or S;

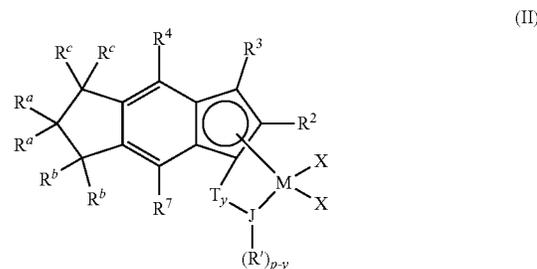
X is a leaving group;

m=1; n=1, 2 or 3; q=1, 2 or 3; and the sum of m+n+q is equal to the oxidation state of the transition metal; and

obtaining a C₃-C₄₀ olefin-ethylene-diene terpolymer comprising from 1 to 35 mol % of ethylene, from 98.9 to 65 mol % C₃-C₄₀ olefin, and from 0.1 to 10 mol % diene.

38

2. The method of paragraph 1, wherein the catalyst compound is represented by formula (II):



where M is a group 4 metal;

J is N, O, S or P;

p is 2 when J is N or P, and is 1 when J is O or S;

each R^a is independently C₁-C₁₀ alkyl;

each R^c is independently hydrogen or a C₁-C₁₀ alkyl;

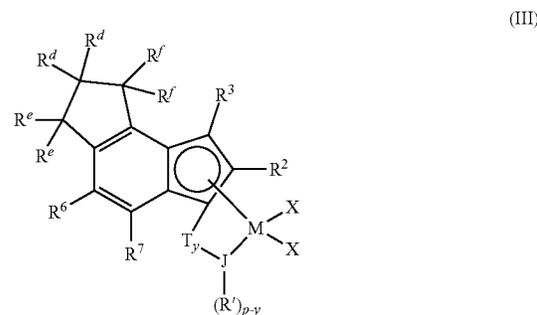
each R², R³, R⁴, and R⁷ is independently hydrogen, or a C₁-C₅₀ substituted or unsubstituted hydrocarbyl, halocarbyl, silylcarbyl or germylcarbyl, provided that: 1) R³ and/or R⁴ are not aryl or substituted aryl, 2) R³ is not directly bonded to a group 15 or 16 heteroatom, and 3) adjacent R⁴, R^c, R^a, R^b, or R⁷ do not join together to form a fused ring system; each Rⁱ is independently a C₁-C₁₀₀ substituted or unsubstituted hydrocarbyl, halocarbyl, silylcarbyl or germylcarbyl;

T is a bridging group and y is 0 or 1 indicating the absence (y=0) or presence (y=1) of T; each X is, independently, a leaving group, or two Xs are joined and bound to the metal atom to form a metallocycle ring, or two Xs are joined to form a chelating ligand, a diene ligand, or an alkylidene.

3. The method of paragraph 2, wherein both R^a are methyl and all R^b and R^c are hydrogen.

4. The method of paragraph 2 or 3, wherein R² is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl or an isomer thereof and R³, R⁴, R², and R⁷ are hydrogen.

5. The method of paragraph 1, wherein the catalyst compound is represented by formula (III):



where M is a group 4 metal;

J is N, O, S or P;

p is 2 when J is N or P, and is 1 when J is O or S;

each R^d, R^e and R^f is independently hydrogen or a C₁-C₁₀ alkyl;

each R², R³, R⁶, and R⁷ is independently hydrogen, or a C₁-C₅₀ substituted or unsubstituted hydrocarbyl, halocarbyl, silylcarbyl or germylcarbyl;

each R' is, independently, a C₁-C₁₀₀ substituted or unsubstituted hydrocarbyl, halocarbyl, silylcarbyl or germylcarbyl;

T is a bridging group and y is 0 or 1 indicating the absence (y=0) or presence (y=1) of T; each X is independently a leaving group, or two Xs are joined and bound to the metal atom to form a metallocycle ring, or two Xs are joined to form a chelating ligand, a diene ligand, or an alkylidene.

6. The method of paragraph 5, wherein both R^d are methyl and all R^e and R^f are hydrogen.

7. The method of paragraph 5 or 6, wherein R² is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl or an isomer thereof and R³, R⁴, R⁶, and R⁷ are hydrogen.

8. The method of any of the above paragraphs 1 to 7, wherein R² is methyl.

9. The method of any of paragraphs 1 to 3, wherein y is 1.

10. The method of any of the above paragraphs 1 to 10, wherein y is 1 and T is (CR⁸R⁹)_x, SiR⁸R⁹, or GeR⁸R⁹ where x is 1 or 2, R⁸ and R⁹ are independently selected from hydrogen or substituted or unsubstituted hydrocarbyl, halocarbyl, silylcarbyl and germylcarbyl and R⁸ and R⁹ may optionally be bonded together to form a ring structure.

11. The method of any of the above paragraphs 1 to 10 wherein, M is Ti.

12. The method of any of the above paragraphs 1 to 11 wherein, J is N.

13. The method of any of the above paragraphs 1 to 12, wherein R' is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, phenyl or an isomer thereof.

14. The method of any of paragraphs 1 to 12, wherein R is t-butyl, neopentyl, cyclohexyl, cyclooctyl, cyclododecyl, adamantyl, or norbornyl.

15. The method of any of the above paragraphs 1 to 13, wherein each X is, independently, selected from hydrocarbyl radicals having from 1 to 20 carbon atoms, aryls, hydrides, amides, alkoxides, sulfides, phosphides, halides, amines, phosphines, ethers, and a combination thereof, (two X's may form a part of a metallocycle ring, or two X's are joined to form a chelating ligand, diene ligand or alkylidene).

16. The method of any of the above paragraphs 1 to 15, wherein each X is independently selected from halides, aryls and C₁ to C₅ alkyl groups.

17. The method of paragraph 1, wherein the catalyst is one or more of: dimethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(t-butylamido)M(R)₂; dimethylsilylene(6,6-dimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(t-butylamido)M(R)₂; dimethylsilylene(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)M(R)₂; dimethylsilylene(7,7-dimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)M(R)₂; dimethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(6,6-dimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(7,7-dimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(cyclohexylamido)M(R)₂; dimethylsilylene(6,6-dimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(cyclohexylamido)M(R)₂; dimethylsilylene(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclohexylamido)M(R)₂; dimethylsilylene(7,7-dimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclohexylamido)M(R)₂; dimethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(adamantylamido)M(R)₂; dimethylsilylene(6,6-

dimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(adamantylamido)M(R)₂; dimethylsilylene(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(adamantylamido)M(R)₂; dimethylsilylene(7,7-dimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(adamantylamido)M(R)₂; dimethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(neopentylamido)M(R)₂; dimethylsilylene(6,6-dimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(neopentylamido)M(R)₂; dimethylsilylene(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(neopentylamido)M(R)₂; dimethylsilylene(7,7-dimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(neopentylamido)M(R)₂; dimethylsilylene(2-methyl-6,6-diethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(t-butylamido)M(R)₂; dimethylsilylene(6,6-diethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(t-butylamido)M(R)₂; dimethylsilylene(2-methyl-7,7-diethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)M(R)₂; dimethylsilylene(7,7-diethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)M(R)₂; dimethylsilylene(2-methyl-6,6-diethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(6,6-diethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(2-methyl-7,7-diethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(7,7-dimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclododecylamido)M(R)₂; diethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(t-butylamido)M(R)₂; diethylsilylene(6,6-dimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(t-butylamido)M(R)₂; diethylsilylene(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)M(R)₂; diethylsilylene(7,7-dimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)M(R)₂; dimethylsilylene(2-methyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclohexylamido)M(R)₂; dimethylsilylene(2-methyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(cyclododecylamido)M(R)₂; dimethylsilylene(2-methyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(adamantylamido)M(R)₂; and dimethylsilylene(2-methyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)M(R)₂; where M is selected from a group consisting of Ti, Zr, and Hf and R is selected from halogen and C₁ to C₅ alkyl.

18. The method of paragraph 1, wherein the catalyst is one or more of: dimethylsilylene(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)titanium dimethyl; or dimethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(t-butylamido)titanium dimethyl.

19. The method of any of the above paragraphs 1 to 18, wherein the activator is represented by the formula:



50 wherein: Z is (L-H) or a reducible Lewis acid, wherein L is a neutral Lewis base, H is hydrogen, and (L-H) is a Bronsted acid; and A^{d-} is a boron containing non-coordinating anion having the charge d-, wherein d is 1, 2, or 3.

20. The method of any of the above paragraphs 1 to 19, wherein the activator comprises one or more of: N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorophenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluorophenyl)borate, [Me₃NH⁺][B(C₆F₅)₄⁻], 1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl)pyrrolidinium; [Me₃NH⁺][B(C₆F₅)₄⁻], 1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl)pyrrolidinium,

sodium tetrakis(pentafluorophenyl)borate, potassium tetrakis(pentafluorophenyl)borate, 4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridinium, sodium tetrakis(perfluorophenyl)aluminate, potassium tetrakis(pentafluorophenyl), and N,N-dimethylanilinium tetrakis(perfluorophenyl)aluminate.

21. The method of any of the above paragraphs 1 to 20, wherein the activator is N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate or N,N-dimethylanilinium tetrakis(perfluorophenyl)borate.

22. The method of any of the above paragraphs 1 to 21, wherein the C₃-C₄₀ olefin is a C₃-C₂₀ α-olefin.

23. The method of any of the above paragraphs 1 to 22, wherein the C₃-C₂₀ α-olefin is one or more of propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene and isomers thereof.

24. The method of any of the above paragraphs 1 to 23, wherein the C₃-C₂₀ α-olefin is propylene.

25. The method of any of the above paragraphs 1 to 24, wherein the diene is one or more of 5-ethylidene-2-norbornene; 1,4-hexadiene; 5-methylene-2-norbornene; 1,6-octadiene; 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; dicyclopentadiene; and combinations thereof.

26. The method of any of the above paragraphs 1 to 25, wherein the diene is 5-ethylidene-2-norbornene.

27. The method of any of the above paragraphs 1 to 26, wherein the catalyst has an efficiency greater than 10,000 g polymer/g catalyst, alternatively greater than 50,000 g poly/g cat, alternatively greater than 150,000 g poly/g cat.

28. The method of any of the above paragraphs 1 to 27, wherein the polymer produced has a propylene tacticity index ratio [m/r] of greater than 0.4 and less than 1.2.

29. The method of any of the above paragraphs 1 to 28, wherein the contacting occurs at a temperature of from 0° C. to 300° C., at a pressure from 0.35 MPa to 16 MPa, alternately from 0.35 MPa to 10 MPa.

30. The method of any of the above paragraphs 1 to 29, wherein the polymer produced has:

- 1) a propylene tacticity index ratio [m/r] of greater than 0.4 and less than 1.2;
- 2) a crystallinity of from 0% to 3%;
- 3) a melt flow rate at 230° C. from 0.2 (preferably 0.5) g/10 min to 100 g/10 min; and
- 4) a glass transition temperature of from -2° C. to -25° C.;

31. The method of paragraph 30, wherein the polymer produced has a g' value of 0.90 or greater.

32. The method of paragraph 30 or 31, wherein the polymer produced has a number average molecular weight value of from 40,000 g/mol to 250,000 g/mol.

33. The method of any of paragraphs 30 to 32, wherein the polymer produced has a weight average molecular weight value of from 50,000 g/mol to 500,000 g/mol.

34. The method of any of paragraphs 30 to 33, wherein the polymer produced has a z-average molecular weight value of from 150,000 g/mol to 800,000 g/mol.

35. The method of any of paragraphs 30 to 34, wherein the polymer produced has an Mw/Mn of from 1.5 to 3.

36. A polymer obtained by the method of any of paragraphs 1 to 35, wherein the polymer having a crystallinity of from 0% to 3%.

37. The polymer of paragraph 36, wherein the polymer has a melt flow rate at 230° C. from 0.5 g/10 min to 100 g/10 min.

38. The polymer of paragraph 36 or paragraph 37, wherein the polymer has a glass transition temperature of from -2° C. to -25° C.

39. The polymer of any of paragraphs 36 to 38, wherein the polymer has a g' value of 0.95 or greater.

40. The polymer of paragraph 39, wherein the polymer has a g' value of 0.98 or greater.

41. The polymer of any of paragraphs 36 to 40, wherein the polymer has an Mw/Mn of from 1.5 to 3, preferably 1.8 to 2.2.

42. The polymer of any of paragraphs 36 to 41, wherein the polymer has a number average molecular weight value of from 40,000 g/mol to 250,000 g/mol.

43. The polymer of any of paragraphs 36 to 42, wherein the polymer has a weight average molecular weight value of from 50,000 g/mol to 500,000 g/mol.

44. The polymer of any of paragraphs 36 to 43, wherein the polymer has a z-average molecular weight value of from 150,000 g/mol to 800,000 g/mol.

45. A C₃-C₄₀ olefin-ethylene-diene terpolymer comprising from 1 to 35 mol % of ethylene, from 98.9 to 65 mol % C₃-C₄₀ olefin, and from 0.1 to 10 mol % diene, wherein the terpolymer has:

- 1) a propylene tacticity index ratio [m/r] of greater than 0.4 and less than 1.2;
- 2) a crystallinity of from 0% to 3%;
- 3) a melt flow rate at 230° C. from 0.5 g/10 min to 100 g/10 min;
- 4) a glass transition temperature of from -2° C. to -25° C.;
- 5) an Mw/Mn of from 1.5 to 3;
- 6) a number average molecular weight value of from 40,000 g/mol to 250,000 g/mol;
- 7) a weight average molecular weight value of from 50,000 g/mol to 500,000 g/mol; and
- 8) a z-average molecular weight value of from 150,000 g/mol to 800,000 g/mol.

46. A C₃-C₄₀-olefin-ethylene-diene terpolymer comprising from 1 to 35 mol % ethylene, from 98.9 to 65 mol % C₃ to C₄₀ comonomer, and from 0.1 to 10 mol % diene, and having a polymer crystallinity of less than 3%; a melt flow rate (at 230° C.) of less than 100 g/10 minutes; a glass transition temperature of from -2° C. to -25° C.; and a propylene tacticity index ratio [m/r] from 0.4 to 1.0.

47. The terpolymer of paragraph 45 or 46, wherein the propylene tacticity index is greater than 0.50 to less than 0.9.

48. The terpolymer of any of paragraphs 45 to 47, wherein the polymer has a g' value of 0.90 or greater.

49. The terpolymer of any of paragraphs 45 to 48, wherein the C₃-C₄₀ olefin is propylene or 1-butene.

50. The terpolymer of any of paragraphs 45 to 48, wherein the C₃-C₄₀ olefin is propylene.

51. The terpolymer of any of paragraphs 45 to 50, wherein the diene is one or more of 5-ethylidene-2-norbornene; 1,4-hexadiene; 5-methylene-2-norbornene; 1,6-octadiene; 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; dicyclopentadiene; and combinations thereof.

52. The terpolymer of any of paragraphs 45 to 50, wherein the diene is one or more of 5-ethylidene-2-norbornene

53. The terpolymer of paragraph any of paragraphs 45 to 52, wherein the polymer has a number average molecular weight value of from 40,000 g/mol to 250,000 g/mol.

54. The terpolymer of any of paragraphs 45 to 53, wherein the polymer has a weight average molecular weight value of from 50,000 g/mol to 500,000 g/mol.

55. The terpolymer of any of paragraphs 45 to 54, wherein the polymer has a z-average molecular weight value of from 150,000 g/mol to 800,000 g/mol.

56. A tire sidewall, a retreaded tire, a truck tire, an off-road tire, a passenger automobile tire, a bus tire, a motorcycle tire, a bicycle tire, or an aircraft tire comprising the polymer of any of paragraphs 45 to 55.

57. A tire tread, adhesive composition, rubber composition, belt, thermoplastic vulcanizate composition, vibration damping device, or bonding agent comprising the polymer of any of paragraphs 45 to 55.

Experimental

Test Methods for Polymers Produced in a Continuous Polymerization Unit:

Ethylene content is determined using FTIR according to the ASTM D3900 and is not corrected for diene content. ENB is determined using FTIR according to ASTM D6047. The content of other diene is obtained using ¹³C NMR.

Molecular Weight, Comonomer Composition and Long Chain Branching Determination by Polymer Char GPC-IR Hyphenated with Multiple Detectors

The distribution and the moments of molecular weight (M_w, M_n, M_w/M_n, etc.), the comonomer content (C₂, C₃, C₆, etc.) and the long chain branching (g') are determined by using a high temperature Gel Permeation Chromatography (Polymer Char GPC-IR) equipped with a multiple-channel band-filter based Infrared detector IR5, an 18-angle light scattering detector and a viscometer. Three Agilent PLgel 10 μm Mixed-B LS columns are used to provide polymer separation. Aldrich reagent grade 1,2,4-trichlorobenzene (TCB) with 300 ppm antioxidant butylated hydroxytoluene (BHT) is used as the mobile phase. The TCB mixture is filtered through a 0.1 μm Teflon filter and degassed with an online degasser before entering the GPC instrument. The nominal flow rate is 1.0 mL/min and the nominal injection volume is 200 μL. The whole system including transfer lines, columns, detectors are contained in an oven maintained at 145° C. Given amount of polymer sample is weighed and sealed in a standard vial with 80 μL flow marker (Heptane) added to it. After loading the vial in the autosampler, polymer is automatically dissolved in the instrument with 8 mL added TCB solvent. The polymer is dissolved at 160° C. with continuous shaking for about 1 hour. The TCB densities used in concentration calculation are 1.463 g/ml at room temperature and 1.284 g/ml at 145° C. The sample solution concentration is from 0.2 to 2.0 mg/ml, with lower concentrations being used for higher molecular weight samples.

The concentration (c), at each point in the chromatogram is calculated from the baseline-subtracted IR5 broadband signal intensity (I), using the following equation:

$$c = \beta I$$

where β is the mass constant determined with PE or PP standards. The mass recovery is calculated from the ratio of the integrated area of the concentration chromatography over elution volume and the injection mass which is equal to the pre-determined concentration multiplied by injection loop volume.

The conventional molecular weight (IR MW) is determined by combining universal calibration relationship with the column calibration which is performed with a series of monodispersed polystyrene (PS) standards ranging from 700 to 10M. The MW at each elution volume is calculated with following equation.

$$\log M = \frac{\log(K_{PS}/K)}{a+1} + \frac{a_{PS}+1}{a+1} \log M_{PS}$$

where the variables with subscript "PS" stands for polystyrene while those without a subscript are for the test samples. In this method, $a_{PS}=0.67$ and $K_{PS}=0.000175$ while a and K are calculated as published in literature (e.g., T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, *Macromolecules*, Volume 34, Number 19, pp. 6812-6820, (2001)), except that for purposes of this invention and claims thereto, unless otherwise indicated, $\alpha=0.695+(0.01*(\text{wt. fraction propylene}))$ and $K=0.000579-(0.0003502*(\text{wt. fraction propylene}))$ for ethylene-propylene copolymers and ethylene-propylene-diene terpolymers, $\alpha=0.695$ and $K=0.000579$ for linear ethylene polymers, $\alpha=0.705$ and $K=0.0002288$ for linear propylene polymers, $\alpha=0.695$ and $K=0.000181$ for linear butene polymers, α is 0.695 and K is $0.000579*(1-0.0087*w2b+0.000018*(w2b)^2)$ for ethylene-butene copolymer where w2b is a bulk weight percent of butene comonomer, a is 0.695 and K is $0.000579*(1-0.0075*w2b)$ for ethylene-hexene copolymer where w2b is a bulk weight percent of hexene comonomer, and a is 0.695 and K is $0.000579*(1-0.0077*w2b)$ for ethylene-octene copolymer where w2b is a bulk weight percent of octene comonomer. Concentrations are expressed in g/cm³, molecular weight is expressed in g/mole, and intrinsic viscosity (hence K in the Mark-Houwink equation) is expressed in dL/g unless otherwise noted. Values used for certain propylene-ethylene-ENB polymers prepared herein are shown below. For purposes of this invention, the wt. fraction propylene for ethylene-propylene and ethylene-propylene-diene polymers is determined by GPC-IR where the "wt. fraction propylene" = $(100 - \text{wt \% ethylene})/100$. Values of wt % ethylene are tabulated in Table 2-part 1 under the column labelled wt % C₂ (IR).

The comonomer composition is determined by the ratio of the IR5 detector intensity corresponding to CH₂ and CH₃ channel calibrated with a series of PE and PP homo/copolymer standards whose nominal value are predetermined by NMR or FTIR. In particular, this provides the methyls per 1000 total carbons (CH₃/1000TC) as a function of molecular weight. The short-chain branch (SCB) content per 1000TC (SCB/1000TC) is then computed as a function of molecular weight by applying a chain-end correction to the CH₃/1000TC function, assuming each chain to be linear and terminated by a methyl group at each end. The weight % comonomer is then obtained from the following expression in which f is 0.3, 0.4, 0.6, 0.8, and so on for C₃, C₄, C₆, C₈, and so on co-monomers, respectively:

$$w2 = f * \text{SCB}/1000\text{TC}$$

The bulk composition of the polymer from the GPC-IR and GPC-4D analyses is obtained by considering the entire signals of the CH₃ and CH₂ channels between the integration limits of the concentration chromatogram. First, the following ratio is obtained

$$\text{Bulk IR ratio} = \frac{\text{Area of CH}_3 \text{ signal within integration limits}}{\text{Area of CH}_2 \text{ signal within integration limits}}$$

Then the same calibration of the CH₃ and CH₂ signal ratio, as mentioned previously in obtaining the CH₃/1000TC as a function of molecular weight, is applied to obtain the bulk CH₃/1000TC. A bulk methyl chain ends per 1000TC (bulk

CH₃end/1000TC) is obtained by weight-averaging the chain-end correction over the molecular-weight range. Then

$$w_{2b} = f_{\text{bulk}} \text{CH}_3/1000TC$$

$$\text{bulk } SCB/1000TC = \text{bulk } CH_3/1000TC - \text{bulk } CH_3\text{end}/1000TC$$

and bulk SCB/1000TC is converted to bulk w₂ in the same manner as described above.

The LS detector is the 18-angle Wyatt Technology High Temperature DAWN HELEOSII. The LS molecular weight (M) at each point in the chromatogram is determined by analyzing the LS output using the Zimm model for static light scattering (M. B. Huglin, LIGHT SCATTERING FROM POLYMER SOLUTIONS, Academic Press, 1971):

$$\frac{K_o c}{\Delta R(\theta)} = \frac{1}{MP(\theta)} + 2A_2 c.$$

Here, $\Delta R(\theta)$ is the measured excess Rayleigh scattering intensity at scattering angle θ , c is the polymer concentration determined from the IR5 analysis, A_2 is the second virial coefficient. $P(\theta)$ is the form factor for a monodisperse random coil, and K_o is the optical constant for the system:

$$K_o = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A}$$

where N_A is Avogadro's number, and (dn/dc) is the refractive index increment for the system. The refractive index, $n=1.500$ for TCB at 145° C. and $\lambda=665$ nm. For analyzing polyethylene homopolymers, ethylene-hexene copolymers, and ethylene-octene copolymers, $dn/dc=0.1048$ ml/mg and $A_2=0.0015$; for analyzing ethylene-butene copolymers, $dn/dc=0.1048*(1-0.00126*w_2)$ ml/mg and $A_2=0.0015$ where w_2 is weight percent butene comonomer. For propylene-ethylene-ENB polymers, $dn/dc=0.104-(0.0016*wt \% \text{ ENB})$, wherein the wt % ENB is measured by FTIR according to ASTM D6047, and $A_2=0.00060$.

A high temperature Agilent (or Viscotek Corporation) viscometer, which has four capillaries arranged in a Wheatstone bridge configuration with two pressure transducers, is used to determine specific viscosity. One transducer measures the total pressure drop across the detector, and the other, positioned between the two sides of the bridge, measures a differential pressure. The specific viscosity, η_s , for the solution flowing through the viscometer is calculated from their outputs. The intrinsic viscosity, $[\eta]$, at each point in the chromatogram is calculated from the following equation:

$$[\eta] = \eta_s / c$$

where c is concentration and was determined from the IR5 broadband channel output. The viscosity MW at each point is calculated from the below equation:

$$M = K_{PS} M^{PS+1} / [\eta].$$

The branching index (g'_{vis}) is calculated using the output of the GPC-IR5-LS-VIS method as follows. The average intrinsic viscosity, of the sample is calculated by:

$$[\eta]_{\text{avg}} = \frac{\sum c_i [\eta]_i}{\sum c_i}$$

where the summations are over the chromatographic slices, i , between the integration limits. The branching index g'_{vis} (also referred to as branching index g') is defined as:

$$g'_{vis} = \frac{[\eta]_{\text{avg}}}{k M_v^\alpha}$$

5

M_v is the viscosity-average molecular weight based on molecular weights determined by LS analysis. α and K are as calculated as published in literature (Sun, T. et al. *Macromolecules* 2001, 34, 6812), except for the α 's and K 's defined above.

All the concentrations are expressed in g/cm³, molecular weight is expressed in g/mole, and intrinsic viscosity is expressed in dL/g unless otherwise noted.

Differential Scanning calorimetry (DSC) was used to determine glass transition temperature (T_g) of the α -olefin-ethylene-diene polymer according to ASTM D3418-03. Melting temperature (T_m), and heat of fusion (H_f) are also determined by DSC. DSC data were obtained using a TA Instruments model Q200 machine. Samples weighing approximately 5-10 mg were kept in an aluminum sample pan and hermetically sealed. These were gradually heated to 200° C. at a rate of 10° C./minute and thereafter, held at 200° C. for 2 minutes. They were subsequently cooled to -90° C. at a rate of 10° C./minute and held isothermally for 2 minutes at -90° C. This was followed by a second heating cycle wherein the samples were heated to 200° C. at 10° C./minute. Both the first and second cycle thermal events were recorded.

During the second heating cycle, appearance of melting indicates crystallinity and thus measured heat of fusion is used to compute the crystallinity. The thermal output, recorded as the area under the melting peak of the sample, is a measure of the heat of fusion and may be expressed in Joules per gram of polymer. The melting point is recorded as the temperature of the greatest heat absorption within the range of melting of the sample relative to a baseline measurement for the increasing heat capacity of the polymer as a function of temperature.

The T_g values reported in the table are the values recorded during the second heating cycle.

The percent crystallinity is calculated using the formula: [area under the curve (in J/g)/H° (in J/g)]*100, where H° is the ideal heat of fusion for a perfect crystal of the homopolymer of the major monomer component. These values for H° are to be obtained from the *Polymer Handbook, Fourth Edition*, published by John Wiley and Sons, New York 1999, except that a value of 290 J/g is used for H° (polyethylene), a value of 140 J/g is used for H° (polybutene), and a value of 207 J/g is used for H° (polypropylene).

Calculation of Tacticity

¹³C NMR Conditions

The ¹³C solution NMR was performed on a 10 mm cryoprobe with a field strength of at least 600 MHz solvent mixture of ODCB (ortho-dichlorobenzene) and benzene-d₆ (C₆D₆) (90:10) at 120° C. with a flip angle of 90° and inverse gated decoupling with a 20 second delay. Sample preparation (polymer dissolution) was performed at 140° C. where 0.20 grams of polymer was dissolved in an appropriate amount of solvent to give a final polymer solution volume of 3 ml. Chemical shifts were referenced to the solvent signal at 127.2 ppm.

The tacticity is calculated from integrating the CH₃ region of the propylene unit where the regions are defined as:

47

mm region	21.20-20.5 ppm
mr region	20.5-19.75 ppm
rr region	19.75-18.7 ppm

To account for the portion of the EP sequence that overlaps in the mr and rr regions, the CH EPE peak at 32.8 ppm and the CH EPP peak at 30.5 ppm were used to remove the EPE and EPP contribution.

mm region	21.20-20.5 ppm
mr region	(20.5-19.75 ppm-CH EPP)
rr region	(19.75-18.7 ppm-CH EPE)

The sum or "total" of the integrals of the mm, mr and rr regions are used to calculate the percentage of mm, mr and rr triads where "total" = mm + mr + rr.

$$\% mm = mm * 100 / \text{total}$$

$$\% mr = mr * 100 / \text{total}$$

$$\% rr = rr * 100 / \text{total}$$

48

	Chemical shift	Mole %	Weight %
C3	$I_{CH3} = 18-23$ ppm	Mole C3 = $I_{CH3} / \text{total} * 100$	Mole C3 * 42 / total * 100
5 C2	Ia = 23-60 ppm	Mole C2 = $[(Ia - 2 * I_{CH3}) / 2] / \text{total} * 100$	Mole C2 * 28 / total * 100
Total		C3 + C2	Mole C3 * 42 + mole C2 * 28

10 with the C2 content determined by ^{13}C NMR being uncorrected for ENB.

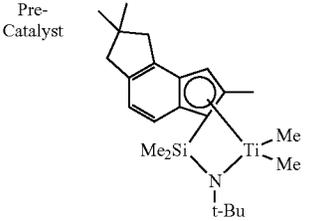
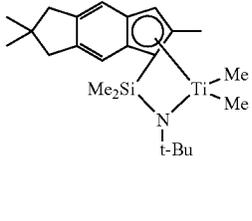
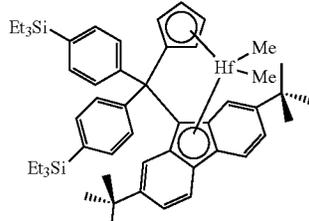
Melt Flow Rate (MFR): MFR is measured according to ASTM D1238 test method, at 230° C. and 2.16 kg load, and is expressed as dg/min or g/10 min.

15 Mooney viscosity (ML) can be determined by ASTM D1646-17 ((1+4), 125° C., 2 s⁻¹ shear rate).

Room temperature is 23° C. unless otherwise noted.

20

Examples

Pre-Catalyst	A	B	C
			
CAT ID	A	B	C
CAT Name	dimethylsilylene(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(tert-butylamido)titanium dimethyl	dimethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(tert-butylamido)titanium dimethyl	[di(p-triethylsilylphenyl)methylene] (cyclopentadienyl) (2,7-di-tert-butylfluoren-9-yl)hafnium dimethyl
Activator	N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate		N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate
ACT ID	A-1		A-2

Regio-defects and ENB sequence effects are not accounted for in the tacticity calculation. Their contribution is assumed to be negligible.

Percent dyad, m and r, are calculated from:

$$m = \% mm + (0.5 * \% mr)$$

$$r = \% rr + (0.5 * \% mr)$$

The "propylene tacticity index", expressed herein as [m/r], is calculated from the corrected integral regions as described above. When [m/r] is 0 to less than 1.0, the polymer is generally described as syndiotactic, when [m/r] is 1.0 the polymer is atactic, and when [m/r] is greater than 1.0 the polymer is generally described as isotactic. Values for the percentages of mm, mr, rr, m, and r, and the "propylene tacticity index [m/r] as described above, are reported in Table 2-part 2.

Composition by ^{13}C NMR

Using ^{13}C NMR, the composition of C2 and C3 are calculated as follows:

45 Dimethylsilylene(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(tert-butylamido)titanium dimethyl (CAT ID A) and dimethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(tert-butylamido)titanium dimethyl (CAT ID B) can be prepared as described in U.S. Pat. No. 9,796,795. 50 [Di(p-triethylsilylphenyl)methylene] (cyclopentadienyl) (2,7-di-tert-butylfluoren-9-yl)hafnium dimethyl, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate and N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate can be purchased from W.R. Grace & Conn. 55

Polymerization Examples

Continuous Reactor Polymerization Examples

60 Reactor Description and Preparation

All examples were produced using a solution process in a 1.0-liter continuous stirred-tank reactor (autoclave reactor). The autoclave reactor was equipped with a stirrer, a water-cooling/steam-heating element with a temperature controller, and a pressure controller. Solvents and monomers were purified by passing through purification columns packed with mol sieves. Isohexane (solvent) was passed through 65

four columns in series whereas ethylene, propylene, and toluene were each purified by passing through two columns in series. Purification columns are regenerated periodically (twice/year) or whenever there is evidence of low catalyst activity. 5-ethylidene-2-norbornene (ENB) was purified in a glove box by passing through a bed of basic alumina under a steady nitrogen gas purge. Tri-n-octylaluminum (TNOAL, available from Sigma Aldrich, Milwaukee, Wis.) solution was diluted to a concentration of 1.843×10^{-6} using iso-

hexane. Isohexane and TNOAL solutions were fed using Pulsar pumps and their flow rate was controlled using a pump calibration curve. Purified propylene, and 5-ethylidene-2-norbornene (ENB) were also fed using Pulsar pumps but their flow rate was controlled using mass-flow controllers. The feed rate of purified ethylene was also regulated using a mass flow controller. Ethylene and propylene combined into a single line before entering a manifold upstream of the reactor. Isohexane, TNOAL solution, and ENB solution lines also combined in a single line before entering the same manifold. The resulting two lines merged further downstream and the combined mixture of monomers and solvent was fed into the reactor using a single tube.

The catalysts used in these examples were Cat. A (MW 403.5 g/mol) and Cat. B (MW 403.5 g/mol). Activators used were N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate (A-1) or N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate (A-2). Both the catalyst and activator were first dissolved in toluene and the solution was kept in an inert atmosphere. The solutions of catalyst and activator

were premixed and fed into the reactor using an ISCO syringe pump. The catalyst to activator feed ratio (molar) was set at 0.98. Tri-n-octylaluminum (TNOAL) solution (available from Sigma Aldrich, Milwaukee, Wis.) was further diluted in isohexane and used as a scavenger.

Composition was controlled by adjusting the feed ratio of the monomers while the molecular weight of the polymer was controlled using temperature. To establish a comparative process, samples were produced with Cat C/A-1 catalyst under identical process conditions. For the experimental catalysts, the temperature was varied from 60° C. to 110° C. to study the effect of reactor temperature on molecular weight. The collected samples were first placed on a boiling-water steam table in a hood to evaporate a large fraction of the solvent and unreacted monomers, and then, dried in a vacuum oven at a temperature of about 90° C. for about 12 hours. The vacuum oven dried samples were weighed to obtain yields. The ethylene and ENB content of the polymer were determined by FTIR. The monomer conversions were calculated using the polymer yield, composition and the amount of monomers fed into the reactor. Catalyst activity (also referred to as catalyst productivity) was calculated based the yield and the feed rate of catalyst. All the reactions were carried out at a gauge pressure of about 2.2 MPa. Melt flow rate (MFR) measurements were made as a proxy for molecular weight.

The process conditions and product properties are summarized in Tables 1 and 2. As shown in Table 1, catalyst efficiencies for catalyst systems of the present disclosure are much greater than efficiency values for the comparative catalyst system (catalyst C/A-1 activator).

TABLE 1

Ethylene-propylene-ENB polymerization runs-run conditions. Reactor pressure (Psig) for all runs was 320. C2 feed rate (g/min) was 0.7 for all runs.									
Ex#	Cat ID	Act ID	Rxx T (° C.)	C3	ENB	Catalyst Feed Rate (mol/min)	Activator Feed Rate (mol/min)	Scavenger Feed Rate (mol/min)	Iso-hexane Feed Rate (g/min)
				Feed Rate (g/min)	Feed Rate (g/min)				
C1	C	A-1	110	15	0.31	4.413E-07	4.503E-07	7.3719E-06	61.0
C2	C	A-1	110	15	0.33	4.413E-07	4.503E-07	7.3719E-06	61.1
C3	C	A-1	110	15	0.47	4.413E-07	4.503E-07	7.3719E-06	61.4
1	A	A-1	60	12	0.31	2.680E-07	2.735E-07	7.3719E-06	61.0
2	A	A-1	70	12	0.31	2.680E-07	2.735E-07	7.3719E-06	61.0
3	A	A-1	80	12	0.31	2.680E-07	2.735E-07	7.3719E-06	61.0
4	A	A-1	80	12	0.31	2.680E-07	2.735E-07	7.3719E-06	61.0
5	A	A-1	90	12	0.31	2.680E-07	2.735E-07	7.3719E-06	61.0
6	A	A-1	100	12	0.31	2.680E-07	2.735E-07	7.3719E-06	61.0
7	A	A-1	110	12	0.33	2.677E-07	2.731E-07	7.3719E-06	61.1
8	A	A-1	110	12	0.31	2.677E-07	2.731E-07	7.3719E-06	61.0
3	A	A-1	110	12	0.31	2.007E-07	2.048E-07	7.3719E-06	61.0
9	A	A-1	110	12	0.31	1.338E-07	1.366E-07	7.3719E-06	61.0
10	B	A-1	70	12	0.31	2.677E-07	2.731E-07	7.3719E-06	61.0
11	B	A-1	80	12	0.31	2.677E-07	2.731E-07	7.3719E-06	61.0
12	B	A-1	80	12	0.31	2.677E-07	2.731E-07	7.3719E-06	61.0
13	B	A-1	90	12	0.31	2.677E-07	2.731E-07	7.3719E-06	61.0
14	B	A-1	100	12	0.31	2.677E-07	2.731E-07	7.3719E-06	61.0
15	B	A-1	100	12	0.33	2.677E-07	2.731E-07	7.3719E-06	61.1
16	B	A-1	100	12	0.33	2.677E-07	2.731E-07	7.3719E-06	61.1
17	B	A-1	100	12	0.33	2.677E-07	2.732E-07	7.3719E-06	61.1
18	B	A-2	80	12	0.33	2.677E-07	2.731E-07	7.3719E-06	61.1
19	B	A-2	90	12	0.33	2.677E-07	2.731E-07	7.3719E-06	61.1
20	B	A-2	90	12	0.33	2.677E-07	2.732E-07	7.3719E-06	61.1
21	B	A-2	100	12	0.33	2.677E-07	2.731E-07	7.3719E-06	61.1

US 11,597,782 B2

51

TABLE 1

Ethylene-propylene-ENB polymerization runs-run conditions.
 Reactor pressure (Psig) for all runs was 320.
 C2 feed rate (g/min) was 0.7 for all runs. (continued)

Ex#	% C2 = Conversion	% C3 = Conversion	% ENB Conversion	Polymer Rate (g/min)	Polymer (wt %), exptal	Cat Efficiency (g poly/ g cat)
C1	24.6	11.9	12.6	2.0	4.63	4802
C2	22.3	11.4	12.0	1.9	4.18	4561
C3	33.0	10.3	11.0	1.8	4.18	4393
1	15.3	10.7	8.7	1.4	2.37	13084
2	11.5	9.9	7.5	1.3	2.34	11928
3	18.0	15.3	12.6	2.0	3.69	18530
4	15.3	10.8	8.8	1.4	2.67	13269
5	15.0	10.9	9.2	1.4	3.03	13315
6	20.7	13.5	12.6	1.8	4.10	16736
7	24.3	14.9	16.9	2.0	4.27	18657
8	27.4	15.7	16.5	2.1	5.34	19676
3	22.1	13.4	13.4	1.8	4.95	22284
9	15.2	8.1	8.1	1.1	2.72	20494
10	28.4	23.7	23.0	3.1	5.58	28889
11	37.0	29.2	30.2	3.9	7.52	35741
12	30.7	24.7	24.3	3.3	6.38	30093
13	32.6	28.0	31.0	3.7	7.46	34167
14	38.3	28.3	31.1	3.8	7.80	34815
15	33.6	25.4	21.7	3.4	6.90	31019
16	37.9	26.2	21.0	3.5	7.09	32222
17	39.0	23.9	20.2	3.2	6.82	29722
18	36.0	24.6	20.8	3.3	5.84	30278
19	35.1	25.3	25.0	3.4	6.36	31111
20	38.3	31.6	28.5	4.2	8.09	38426
21	33.8	20.9	22.6	2.8	6.21	26111

52

TABLE 2

Ethylene-propylene-ENB polymerization runs-polymer properties-part 1. (continued)

Ex#	Mz (LS)	g' (Vis Avg)	Mn (Vis)	Mw (Vis)	Mz (Vis)	IV Bulk (dl/g)
C1	292,680	1.13	64,205	149,432	307,719	1.26
C2	296,914	1.09	62,265	145,343	318,983	1.22
C3	312,554	1.07	59,920	140,243	298,702	1.23
1	751,032	1.09	157,935	376,780	740,684	2.51
2	520,472	1.10	123,410	273,921	506,620	1.96
3						
4						
5						
6						
7	99,728	1.04	28,160	62,549	110,132	0.63
8	100,643	1.01	26,513	60,715	106,603	0.61
3	119,221	1.04	27,666	64,617	115,097	0.64
9	110,644	1.04	28,664	65,765	114,374	0.66
10	449,365	1.14	113,801	255,249	456,362	1.91
11						
12						
13	193,566	1.10	49,273	114,265	210,252	0.99
14						
15	160,765	1.02	37,010	89,037	162,602	0.84
16	133,426	1.02	33,695	81,401	150,975	0.79
17	155,139	1.06	40,023	92,547	172,360	0.85
18	994,218	1.11	202,548	516,830	1,088,585	3.26
19	572,797	1.10	105,682	321,251	629,066	2.22
20	581,862	1.11	140,311	344,188	648,124	2.32
21	454,627	1.08	103,808	252,852	488,323	1.84

TABLE 2

Ethylene-propylene-ENB polymerization runs-polymer properties-part 1.

Ex#	Mn (IR)	Mw (IR)	Mz (IR)	Mw/Mn (IR)	wt % C2 (IR)	Mn (LS)	Mw (LS)
C1	75,692	164,484	304,401	2.17	10.3	73,543	155,205
C2	72,518	158,495	298,413	2.19	10.6	76,527	153,903
C3	70,452	153,124	283,658	2.17	10.8	74,792	158,717
1	194,827	422,757	728,669	2.17	10.2	219,272	439,489
2	145,953	306,677	528,190	2.10	8.7	157,582	309,245
3							
4	108,235	233,042	412,366	2.15	8.9		
5	81,057	170,562	291,286	2.10	9.4		
6							
7	30,711	64,665	106,995	2.11	9.5	29,181	64,236
8	29,579	62,902	104,205	2.13	9.2	31,534	64,860
3	30,796	66,818	112,144	2.17	9.7	30,406	67,003
9	31,310	38,377	112,870	2.18	10.2	31,911	68,793
10	137,067	288,616	482,577	2.11	9.1	148,158	286,578
11							
12	101,589	213,940	357,805	2.11	8.8		
13	55,786	123,235	206,858	2.21	8.9	56,903	120,075
14	43,825	94,066	171,459	2.15	9.3		
15	42,264	94,621	159,737	2.24	9.2	46,246	97,933
16	39,630	86,631	147,380	2.19	9.5	41,949	88,039
17	45,164	97,274	167,715	2.15	9.7	47,190	98,358
18	259,548	582,778	1,028,235	2.25	9.6	297,542	621,594
19	130,671	354,673	620,961	2.71	9.3	136,566	357,313
20	172,608	379,086	642,465	2.20	9.0	187,269	379,997
21	124,017	275,266	479,181	2.22	10.1	141,984	278,970

TABLE 2

Ethylene-propylene-ENB polymerization runs-polymer properties-part 2.												
* MFR too high to measure, ** MFR too low to measure.												
Ex#	C2		Tg (° C.)	MFR (g/10 min)	mm	mr	rr	m	r	m/r	C3	C2
	(wt. % by FTIR) uncorrected	ENB (wt. % by FTIR)									(wt. % by 13C NMR)	(wt. % by 13C NMR)
C1	8.8	2.0	-12.31	5.84	0.13	0.22	0.65	0.24	0.76	0.32	92.5	7.5
C2	8.4	2.1	-12.15	6.53	0.17	0.19	0.63	0.27	0.73	0.37	92.1	7.9
C3	13.0	2.8		6.73								
1	7.7	1.9	-10.85	0.15								
2	6.3	1.8	-11.65	0.81								
3	6.4	2.0	-11.21	2.93								
4	7.6	1.9	-11.48	3.76	0.32	0.31	0.38	0.48	0.54	0.89	91.6	8.5
5	7.5	2.0	-12.7	10.73	0.28	0.31	0.41	0.44	0.57	0.77	91.5	8.5
6	8.2	2.2	-13.58	52.14								
7	8.7	2.8		*								
8	9.2	2.4		*								
3	8.8	2.3		*								
9	9.8	2.3		*								
10	6.5	2.3	-11.25	0.73								
11	6.9	2.4	-10.13	3.33								
12	6.8	2.3	-10.37	3.99	0.22	0.31	0.46	0.38	0.62	0.61	91.8	8.2
13	6.4	2.6	-10.56	19.30								
14	7.3	2.6	-11.66	92.77	0.21	0.32	0.47	0.37	0.63	0.59	91.0	9.0
15	7.2	2.2		53.01								
16	7.8	2.0		111.98								
17	8.7	2.1		*								
18	7.9	2.1		**								
19	7.5	2.5		0.26								
20	6.6	2.3		0.22								
21	8.6	2.7		4.42								

* too high to measure

** too low to measure

From Table 2-part 2, is clearly seen that the inventive polymers have a propylene tacticity index ratio [m/r] greater than the comparative polymers. The inventive polymers are more atactic in nature since [m/r] is closer to one vs. the comparative polymers which are more syndiotactic since [m/r] is closer to zero.

Small Scale Polymerization Reactions:

High Throughput Polymerization Examples

Solutions of the pre-catalysts were made using toluene (ExxonMobil Chemical Company anhydrous, stored under N₂) (98%). Pre-catalyst solutions were typically 0.5 mmol/L.

Solvents, polymerization grade toluene and/or isohexanes were supplied by ExxonMobil Chemical Co. and are purified by passing through a series of columns: two 500 cc Oxiclear cylinders in series from Labclear (Oakland, Calif.), followed by two 500 cc columns in series packed with dried 3 Å molecular sieves (8-12 mesh; Aldrich Chemical Company), and two 500 cc columns in series packed with dried 5 Å molecular sieves (8-12 mesh; Aldrich Chemical Company).

Polymerization grade propylene was used and further purified by passing it through a series of columns: 2250 cc Oxiclear cylinder from Labclear followed by a 2250 cc column packed with 3 Å molecular sieves (8-12 mesh; Aldrich Chemical Company), then two 500 cc columns in series packed with 5 Å molecular sieves (8-12 mesh; Aldrich Chemical Company), then a 500 cc column packed with Selexsorb CD (BASF), and finally a 500 cc column packed with Selexsorb COS (BASF).

Activation of the pre-catalysts was either by N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate or N,N-dimethylanilinium tetrakis(perfluorophenyl)borate (Albemarle Corp). Dimethylanilinium tetrakis(perfluorophenyl)borate and dimethylanilinium tetrakis(perfluoronaphthyl)

borate were typically used as a 5 mmol/L solution in toluene. Tri-n-octylaluminum (TNOAL, Neat, AkzoNobel) was also used as a scavenger prior to introduction of the activator and pre-catalyst into the reactor. TNOAL was typically used as a 5 mmol/L solution in toluene.

Reactor Description and Preparation

Polymerizations were conducted in an inert atmosphere (N₂) drybox using autoclaves equipped with an external heater for temperature control, glass inserts (internal 22.5 mL), septum inlets, regulated supply of nitrogen, ethylene and propylene, and equipped with disposable PEEK mechanical stirrers (800 RPM). The autoclaves were prepared by purging with dry nitrogen at 110° C. or 115° C. for 5 hours and then at 25° C. for 5 hours.

Propylene Polymerization (PP)

The reactor was prepared as described above, then heated to 40° C., and then purged with propylene gas at atmospheric pressure. Isohexanes, ENB and scavenger (TNOAL, 0.5 μmol) were added via syringe. The propylene (1 ml) was condensed into the reactors. The reactor was then brought to process temperature (100° C.) while stirring at 800 RPM. The activator solution, followed by the pre-catalyst solution, were injected via syringe to the reactor at process conditions. Reactor temperature was monitored and typically maintained within +/-1° C. Polymerizations were halted by addition of approximately 50 psi CO₂/Ar (50:50) gas mixture to the autoclaves for approximately 30 seconds. The polymerizations were quenched based on a predetermined pressure loss of approximately 8 psi (max quench value in psi) or for a maximum of 30 minutes polymerization time. The reactors were cooled and vented. Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076) (12.5 mg) was added to each reaction as a toluene solution. The polymers were isolated after the solvent was removed in-vacuo. The actual quench time(s) and max quench value

(psi) are reported. Yields reported include total weight of polymer, residual catalyst, and Irganox 1076. Catalyst activity is reported as grams of polymer per mmol transition metal compound per hour of reaction time (g/mmol·hr). Results are reported in Table 3.

High Throughput Polymer Characterization

For analytical testing, polymer sample solutions were prepared by dissolving polymer in 1,2,4-trichlorobenzene (TCB, 99+% purity from Sigma-Aldrich) containing 2,6-di-tert-butyl-4-methylphenol (BHT, 99% from Aldrich) at 165° C. in a shaker oven for approximately 3 hours. The typical concentration of polymer in solution was between 0.1 to 0.9 mg/mL with a BHT concentration of 1.25 mg BHT/mL of TCB. Samples were cooled to 135° C. for testing.

High temperature size exclusion chromatography was performed using an automated "Rapid GPC" system as described in U.S. Pat. Nos. 6,491,816; 6,491,823; 6,475,391; 6,461,515; 6,436,292; 6,406,632; 6,175,409; 6,454,947; 6,260,407; and 6,294,388; each of which is incorporated herein by reference. Molecular weights (weight average molecular weight (Mw), number average molecular weight (Mn), z-average molecular weight (Mz)) and molecular weight distribution (MWD=Mw/Mn), which is also sometimes referred to as the polydispersity index (PDI) of the polymer, were measured by Gel Permeation Chromatography using a Symyx Technology GPC equipped with dual wavelength infrared detector and calibrated using polystyrene standards (Polymer Laboratories: Polystyrene Calibration Kit S-M-10: Mp (peak Mw) between 580 and 3,039,000). Samples (250 µL of a polymer solution in TCB were injected into the system) were run at an eluent flow rate of 2.0 mL/minute (135° C. sample temperatures, 165° C.

oven/columns) using three Polymer Laboratories: PLgel 10 µm Mixed-B 300×7.5 mm columns in series. No column spreading corrections were employed. Numerical analyses were performed using Epoch® software available from Symyx Technologies or Automation Studio software available from Freeslate. The molecular weights obtained are relative to linear polystyrene standards. Molecular weight data is reported in Table 3 under the headings Mn, Mw, Mz and PDI as defined above.

Differential Scanning calorimetry (DSC) measurements were performed on a TA-Q100 instrument to determine the melting point of the polymers. Samples were pre-annealed at 220° C. for 15 minutes and then allowed to cool to room temperature overnight. The samples were then heated to 220° C. at a rate of 100° C./minute and then cooled at a rate of 50° C./minute. Melting points were collected during the heating period. In all cases, the polymer in Table 3 exhibited no or negligible melting points.

For calculation of ENB: For propylene-ENB copolymers, polymer composition analysis was determined by ¹H NMR using at least a 500 MHz instrument run with a single 30° flip angle RF pulse, 512 scans with a delay of 15 seconds between pulses. The polymer sample was dissolved in heated d₂-1,1,2,2-tetrachloroethane or ODCB/C₆D₆ 90/10 mix and signal collection took place at 120° C.

For calculation of ENB:

$$I_{major} = \text{Integral of major ENB species from 5.2-5.4 ppm}$$

$$I_{minor} = \text{Integral of minor ENB species from 4.6-5.12 ppm}$$

$$I_{eth} = (\text{Integral of } -CH_2- \text{ from 0-3 ppm})$$

Peak Assignments	Intensity of species	MOLE %	WEIGHT %
Olef: 5.3 and 5.1 ppm ENB EP: 3-0 ppm	ENB = $I_{major} + I_{minor}$ EP = $(I_{eth} - 11 * ENB) / 2$	ENB*100/total EP*100/total	ENB*120*100/total wt EP*14*100/total wt

$$\text{total} = (ENB + EP)$$

$$\text{total wt} = (ENB * 120 + EP * 14)$$

Polymerization results are shown in Table 3 below. "Ex #" stands for example number. Examples starting with a "C" are comparative examples. "Cat ID" identifies the pre-catalyst used in the experiment. Corresponding numbers identifying the pre-catalyst are located above. "Act ID" identifies the activator used. "A-1" corresponds to dimethylanilinium tetrakis(perfluorophenyl)borate, and "A-2" corresponds to dimethylanilinium tetrakis(perfluoronaphthyl)borate. For all experiments using borate activators A-1 or A-2, the molar ratio of activator:pre-catalyst was 1.1. "Yield" is polymer yield, and is not corrected for catalyst residue. "Quench time (s)" is the actual duration of the polymerization run in seconds. "Quench Value (psi)" for propylene based runs indicates the maximum set pressure loss (conversion) during the polymerization.

TABLE 3

Propylene ENB copolymerization runs									
Ex#	Cat ID	Act ID	ENB (uL)	Isohexane (uL)	Toluene (uL)	quench value (psi)	quench time (s)	yield (g)	Activity (g P/ mmol cat.hr)
C4	C	A-1	5	4549	445	8.1	130	0.1489	25,771
C5	C	A-1	8	4535	457	8.1	145	0.1297	20,126

TABLE 3-continued

Propylene ENB copolymerization runs									
C6	C	A-1	11	4512	476	8.1	213	0.1000	10,563
C7	C	A-1	17	4479	504	5.3	1801	0.0732	914
C8	C	A-1	25	4428	546	1.8	1801	0.0445	556
C9	C	A-1	38	4352	610	0.6	1803	0.0332	414
23	A	A-1	5	4550	445	8.1	96	0.0864	20,250
24	A	A-1	8	4535	457	8.1	107	0.1547	32,530
25	A	A-1	11	4512	476	8.1	168	0.1369	18,335
26	A	A-1	17	4479	504	8.1	217	0.1163	12,059
27	A	A-1	25	4428	546	8.1	320	0.1054	7,411
28	A	A-1	38	4352	610	8.1	559	0.0959	3,860
29	B	A-1	5	4550	445	8.4	71	0.1855	58,785
30	B	A-1	8	4535	457	8.1	89	0.1626	41,107
31	B	A-1	11	4512	476	8.1	115	0.1448	28,330
32	B	A-1	17	4479	504	8.1	182	0.1227	15,169
33	B	A-1	25	4428	546	8.1	345	0.1037	6,763
34	B	A-1	38	4352	610	8.1	506	0.1072	4,767
35	B	A-1	5	4550	445	8.2	60	0.1876	70,350
36	B	A-1	5	4550	445	8.2	76	0.1733	51,306
37	B	A-1	8	4535	457	8.1	83	0.1662	45,054
38	B	A-1	8	4535	457	8.1	101	0.1624	36,178
39	B	A-1	11	4512	476	8.2	114	0.1429	28,204
40	B	A-1	11	4512	476	8.1	138	0.1377	22,451
41	B	A-1	17	4479	504	8.1	151	0.1270	18,924
42	B	A-1	17	4479	504	8.1	249	0.1115	10,075
43	B	A-1	25	4428	546	8.1	234	0.1056	10,154
44	B	A-1	25	4428	546	8.1	310	0.1049	7,614
45	B	A-1	38	4352	610	8.1	476	0.1063	5,025
46	B	A-1	38	4352	610	8.1	568	0.0970	3,842
47	B	A-2	5	4550	445	8.1	86	0.1594	41,703
48	B	A-2	5	4550	445	8.1	103	0.1611	35,192
49	B	A-2	8	4535	457	8.1	99	0.1470	33,409
50	B	A-2	8	4535	457	8.1	109	0.1482	30,592
51	B	A-2	11	4512	476	8.1	152	0.1198	17,734
52	B	A-2	11	4512	476	8.1	164	0.1241	17,026
53	B	A-2	17	4479	504	8.1	227	0.1118	11,081
54	B	A-2	17	4479	504	8.1	254	0.1108	9,815
55	B	A-2	25	4428	546	8.1	369	0.1152	7,024
56	B	A-2	25	4428	546	8.1	408	0.1009	5,564
57	B	A-2	38	4352	610	8.1	684	0.1029	3,385
58	B	A-2	38	4352	610	8.1	794	0.0993	2,814
C10	C	A-1	5	4549	445	8.1	120	0.1239	23,231
C11	C	A-1	5	4549	445	8.2	140	0.1396	22,436
C12	C	A-1	8	4535	457	8.1	128	0.1042	18,316
C13	C	A-1	8	4535	457	8.1	171	0.1163	15,303
C14	C	A-1	11	4512	476	8.1	183	0.0910	11,189
C15	C	A-1	11	4512	476	8.1	289	0.0926	7,209
C16	C	A-1	17	4479	504	5.0	1800	0.0672	840
C17	C	A-1	17	4479	504	4.0	1800	0.0651	814
C18	C	A-1	25	4428	546	2.1	1800	0.0442	553
C19	C	A-1	25	4428	546	1.5	1800	0.0413	516
C20	C	A-1	38	4352	610	0.6	1801	0.0285	356
C21	C	A-1	38	4352	610	0.8	1801	0.0288	360
C22	C	A-2	5	4549	445	8.1	126	0.1134	20,250
C23	C	A-2	5	4549	445	8.1	156	0.1326	19,125
C24	C	A-2	8	4535	457	8.1	204	0.0916	10,103
C25	C	A-2	8	4535	457	8.1	210	0.1058	11,336
C26	C	A-2	11	4512	476	6.0	1801	0.0739	923
C27	C	A-2	11	4512	476	6.4	1801	0.0825	1,031
C28	C	A-2	17	4479	504	2.6	1801	0.0509	636
C29	C	A-2	17	4479	504	2.3	1801	0.0536	670
C30	C	A-2	25	4428	546	1.2	1800	0.0363	454
C31	C	A-2	25	4428	546	0.3	1800	0.0320	400
C32	C	A-2	38	4352	609	0.9	1800	0.0235	294
C33	C	A-2	38	4352	609	0.8	1801	0.0274	342

Ex#	Mn	Mw	Mz	PDI	ENB wt % (¹ H NMR)
C4	140,223	171,024	345,593	1.64	0.9
C5	126,085	191,984	351,695	1.52	1.3
C6	115,456	184,958	365,078	1.60	1.9
C7	114,128	169,387	298,145	1.48	3.2
C8	91,903	141,804	249,789	1.54	4.6
C9					
23	40,791	62,051	119,512	1.52	0.9
24	38,672	65,924	134,734	1.70	1.1
25	43,741	65,295	116,877	1.49	2.1

TABLE 3-continued

Propylene ENB copolymerization runs					
26	41,389	67,783	144,839	1.64	2.8
27	46,675	65,590	128,566	1.49	4.1
28	43,959	64,116	118,526	1.46	6.5
29	31,024	52,906	117,298	1.71	1.1
30	32,819	53,701	104,765	1.64	1.4
31	32,736	56,085	113,927	1.71	2.3
32	39,706	57,862	102,605	1.46	3.5
33	32,790	51,110	95,472	1.56	5.2
34	33,652	53,463	105,402	1.59	7.3
35	24,492	47,353	113,112	1.93	0.7
36	27,992	50,875	106,440	1.82	
37	25,153	44,518	90,021	1.77	1.1
38	28,547	51,837	107,601	1.82	
39	23,346	47,593	106,139	2.04	1.7
40	27,148	56,173	137,987	2.07	
41	26,402	51,116	111,359	1.94	2.9
42	22,774	45,717	104,937	2.01	
43	28,740	51,624	106,190	1.80	4.1
44	27,772	51,621	107,839	1.86	
45	25,925	47,845	97,198	1.85	5.8
46	28,149	50,779	104,808	1.80	
47	77,160	143,666	325,088	1.86	0.8
48	79,347	143,624	313,675	1.81	
49	89,651	153,234	313,955	1.71	1.2
50	95,418	162,566	357,369	1.70	
51	79,450	143,223	300,178	1.80	2.0
52	87,195	150,589	303,290	1.73	
53	87,290	147,034	312,666	1.68	3.1
54	71,586	133,141	280,051	1.86	
55	79,504	143,222	300,013	1.80	4.3
56	80,046	134,235	272,904	1.68	
57	69,149	118,748	239,010	1.72	6.3
58	67,471	116,000	231,876	1.72	
C10	95,949	181,146	400,744	1.89	0.5
C11	96,682	188,410	453,233	1.95	
C12	93,314	171,044	343,477	1.83	
C13	113,469	189,293	395,617	1.67	
C14	113,414	185,125	365,143	1.63	1.2
C15	109,996	190,949	396,995	1.74	
C16	108,474	184,230	392,700	1.70	1.9
C17	99,235	175,424	401,839	1.77	
C18	102,550	166,064	327,512	1.62	
C19	90,054	151,199	308,109	1.68	
C20	48,805	119,896	300,617	2.46	
C21	64,928	112,524	217,682	1.73	
C22	135,118	240,826	543,428	1.78	0.6
C23	131,283	220,975	439,294	1.68	
C24	111,451	219,433	458,889	1.97	
C25	139,569	243,583	538,854	1.75	
C26	121,332	215,704	459,813	1.78	1.5
C27	119,214	221,250	459,032	1.86	
C28	99,536	183,772	375,852	1.85	2.5
C29	122,299	206,902	476,984	1.69	
C30	82,255	155,863	345,173	1.89	
C31	77,028	138,757	283,386	1.80	
C32	62,881	123,534	276,170	1.96	
C33	74,528	129,516	277,923	1.74	

Catalyst/Activator molar ratio = 1:1; Tri-n-octylaluminum 0.5 umol used as a scavenger; 1 ml propylene; reaction temperature 100° C.; stir speed 800 rpm; reaction was quenched at a pressure drop of 8 psid or 30 minutes, whichever occurred first.

FIG. 1 is a graph illustrating catalyst activity of catalysts A and B versus catalyst C at various levels of ENB in a propylene-ENB copolymerization using N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate (A-1) as the activator. As shown in FIG. 1, catalyst B (dimethylsilylene (2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(t-butylamido)Ti(CH₃)₂) has a productivity of about 30,000 gP/mmol catalyst/hour at ENB levels of 11 uL or less. These levels of productivity are much higher than the comparative catalyst C. Productivity of the catalyst B is also higher than the comparative catalyst C at higher levels of ENB. Similarly, the Catalyst A (μ -(CH₃)₂Si(2,7,7-trimethyl-3,6,7,8-tetrahydro-as-indacen-3-yl)(t-butylamido)Ti(CH₃)₂) has

much higher activity levels than the comparative catalyst system at ENB levels greater than 5 uL.

FIG. 2 is a graph illustrating catalyst activity catalyst B versus catalyst C at various levels of ENB in a propylene-ENB copolymerization using N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate (A-2) as the activator. As shown in FIG. 2, catalyst B (dimethylsilylene(2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(t-butylamido)Ti (CH₃)₂) paired with A-2 activator provides a catalyst activity of about 30,000 gP/mmol catalyst/hour at ENB levels of 10 uL or less. This level of catalyst activity is much higher than that of comparative catalyst C.

FIG. 3 is a graph illustrating Mn values versus levels of ENB of propylene-ENB polymer products according to the

61

polymerizations of Table 3. As shown in FIG. 3, activator N,N-dimethylanilinium tetrakis (perfluoronaphthyl)borate (A-2) more than double the Mn for propylene-ENB polymers formed by catalyst B. Mn values for polymers formed by the catalyst B/A-2 catalyst pair are comparable to Mn values of the polymers formed by catalyst C/A-1 and catalyst C/A-2 catalyst systems. Furthermore, Mn values for polymers formed by the catalyst B/A-2 catalyst pair are from about 70,000 to about 100,000 across a wide range of ENB levels (5 μ L-38 μ L).

Overall, catalyst systems and methods of the present disclosure provide formation of olefin-ethylene-diene polymers (such as propylene-ethylene-ENB terpolymers) at increased activity levels (e.g., 30,000 gP/mmol cat.hr or greater) and efficiency levels (e.g., 5,000 g polymer/g catalyst or greater) while maintaining or improving other polymer properties (such as Mn), as compared to conventional catalyst systems that produce propylene-ethylene-diene terpolymers.

All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while some embodiments of the present disclosure have been illustrated and described, various modifications can be made without departing from the spirit and scope of the present disclosure. Accordingly, it is not intended that embodiments of the present disclosure be limited thereby. Likewise, the term "comprising" is considered synonymous with the term "including." Likewise, whenever a composition, an element or a group of elements is preceded with the transitional phrase "comprising", it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of," "consisting of", "selected from the group of consisting of," or "is" preceding the recitation of the composition, element, or elements and vice versa. Likewise, the terms "comprising," "consisting essentially of," "consisting of" also include the product of the combinations of elements listed after the term.

What is claimed is:

1. A C₃-C₄₀ olefin-ethylene-diene terpolymer comprising from 1 to 35 mol % of ethylene, from 98.9 to 65 mol % C₃-C₄₀ olefin, and from 0.1 to 10 mol % diene, wherein the terpolymer has:

- 1) a C₃₊ olefin tacticity index ratio [m/r] of greater than 0.4 and less than 1.2;
- 2) a crystallinity of from 0% to 3%;

62

- 3) a melt flow rate at 230° C. from 0.5 g/10 min to 100 g/10 min;
- 4) a glass transition temperature of from -2° C. to -25° C.;
- 5) an Mw/Mn of from 1.5 to 3;
- 6) a number average molecular weight value of from 40,000 g/mol to 250,000 g/mol;
- 7) a weight average molecular weight value of from 50,000 g/mol to 500,000 g/mol; and
- 8) a z-average molecular weight value of from 150,000 g/mol to 800,000 g/mol.

2. A C₃-C₄₀-olefin-ethylene-diene terpolymer comprising from 1 to 35 mol % ethylene, from 98.9 to 65 mol % C₃-C₄₀ olefin, and from 0.1 to 10 mol % diene, and having a polymer crystallinity of from 0% to 3%; a melt flow rate (at 230° C.) of from 0.2 g/10 min to 100 g/10 min; a glass transition temperature of from -2° C. to -25° C.; and a C₃₊ olefin tacticity index ratio [m/r] of greater than 0.4 and less than 1.2.

3. The terpolymer of claim 2, wherein the C₃₊ olefin tacticity index ratio is greater than 0.50 to less than 0.9.

4. The terpolymer of claim 2, wherein the polymer has a g' value of 0.90 or greater.

5. The terpolymer of claim 2, wherein the C₃-C₄₀ olefin is propylene or 1-butene.

6. The terpolymer of claim 2, wherein the C₃-C₄₀ olefin is propylene.

7. The terpolymer of claim 2, wherein the diene is one or more of 5-ethylidene-2-norbornene; 1,4-hexadiene; 5-methylene-2-norbornene; 1,6-octadiene; 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; dicyclopentadiene; and combinations thereof.

8. The terpolymer of claim 2, wherein the diene is one or more of 5-ethylidene-2-norbornene.

9. The terpolymer of claim 2, wherein the polymer has a number average molecular weight value of from 40,000 g/mol to 250,000 g/mol.

10. The terpolymer of claim 2, wherein the polymer has a weight average molecular weight value of from 50,000 g/mol to 500,000 g/mol.

11. The terpolymer of claim 2, wherein the polymer has a z-average molecular weight value of from 150,000 g/mol to 800,000 g/mol.

* * * * *